PROBLEMS

IN

PRACTICAL CHEMISTRY

FOR ADVANCED STUDENTS

BY

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WITH TWENTY-TWO DIAGRAMS

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PREFACE

THIS book is intended for the use of advanced students in secondary and technical schools and colleges.

It aims at providing a series of exercises in the form of problems. One of its main objects is to give dexterity in the usual manipulations, and in devising and setting up apparatus. In the author's experience, this dexterity is often sadly wanting in students who would otherwise be good chemists. With this object in view, the time necessary for each problem has been appended, so that the worker can see for himself how he is progressing in the required direction. The times given apply only to the actual experimental work, and do not include time that may be spent in thinking over a problem before carrying it out.

It is hoped that the book will be found very useful to candidates for the Oxford and Cambridge Joint certificates, for London Intermediate Science pass and honours, and that it will not be out of place in the hands of a candidate for a degree. It will also be useful to candidates for science scholarships at the Universities.

It should also be of considerable help to both students and demonstrators in crowded or understaffed laboratories, where much personal attention from the demonstrator is not to be had. The explanations given in the Appendix aim at

providing a substitute for this attention, and at the same time an attempt has been made to avoid "spoon-feeding" the student, by leaving considerable detail to his own ingenuity.

I am indebted to Dr. Baker, D. H. Nagel, Esq., and A. F. Walden, Esq., all of Oxford, for kind permission to use several problems.

G. F. H.

Nottingham.

PROBLEMS IN PRACTICAL CHEMISTRY

INTRODUCTION

EACH experiment should be worked as carefully as possible, and the student should *not* be satisfied till he has arrived at a reasonable result. Notes should be made at the time of the experiment, and should be amplified afterwards It is claimed that a good note-book made from experiments in this book will be of the greatest value to the student.

Students should try to work out problems by methods which they have devised themselves, before turning to the Appendix for details. Where such details are absolutely necessary for guidance, they are given with the problem.

After most experiments or problems is put the time necessary to carry them out properly. If this time is much exceeded, it means that the student is lacking in dexterity and manipulation of apparatus. It is one of the aims of this book to correct this defect.

Elaborate apparatus should be avoided. Aim at apparatus as simple as is consistent with accuracy, and let it be designed for quickness of working also. For example, if the products of a distillation with caustic soda are to be identified, it is generally sufficient to carry out the distillation in a boiling tube, fitted with a right-angled delivery tube, leading into a small flask cooled under the tap. Gases may be simply tested by holding a drop of the reagent on a glass rod in the tube in which the gas is being

generated (*e.g.* lime water for carbon dioxide, water for silicon fluoride, etc.).

A precipitate on a filter-paper may be dried conveniently and quickly by spreading out the filter on a clock-glass which covers a beaker or tin of gently-boiling water.

Finally, too much stress cannot be laid on neatness of working. Do not have bottles and stoppers all over your bench, and if any liquid is spilt on the bench, wipe it up at once. Neatness is at first far more essential than speed. The latter will come by practice, but untidiness in working, if once acquired, is extremely difficult to correct.

Experimental accuracy.

No results will be more accurate than the least accurate portion of the experiment. In general, volumetric problems are easily carried out with an accuracy of ·5 to ·25 per cent. In such cases, the atomic weights used should be accurate to within this limit. For instance, taking O = 16, H should be taken as 1·01 (actual value 1·008); or the inaccuracy is nearly 1 per cent. if H is taken as = 1, whereas experimental accuracy in both volumetric and gravimetric exercises is much greater. For preparations, on the other hand, such accuracy is by no means necessary. Make up your mind, before starting an experiment, what your greatest experimental error is going to be, and see that you do not exceed this error in allowances, rounding off numbers, approximate atomic weights, etc. The atomic weights given in this book are correct to within ·25 per cent., and should therefore be used in all careful volumetric work. In short, the points to be noted are—

(i) Do not spoil accurate experiment by careless calculation.

(ii) Do not perform laborious calculations for merely approximate experimental accuracy

PART I

PRELIMINARY EXERCISES

A FEW TYPICAL INORGANIC PREPARATIONS

THE following examples are merely intended as typifying the preparation of acids, bases, and salts, etc., and must not be regarded as anything like a complete course of inorganic preparations. They are intended to give practice in manipulation.

(A) RECRYSTALLISATION.

Given some commercial oxalic acid, purify it by recrystallising from water as follows. To 200 c.c. of boiling distilled water in a porcelain basin add gradually the powdered acid till no more will dissolve. Filter whilst hot through a funnel kept hot in the water-bath intended for this purpose, and cool the filtrate *rapidly*, with constant stirring.

Drain the fine crystals on the filter-pump, and dissolve them in the least possible quantity of boiling distilled water. Do this by putting them into a dish with a little hot water, boil and add boiling water till solution is just effected. Cool as before, drain the crystals as well as possible on the pump, and dry by wrapping in a sheet of bibulous paper and putting under a weight for 24 hours. [Time required, 40 mins.]

N.B.—When *purifying* a substance by crystallisation aim at getting the crystals as small as possible by rapidly cooling

and stirring the liquor. Small crystals are less liable to enclose portions of the mother liquor, and are more easily drained from it than large ones.

(B) PREPARATION OF SIMPLE SALTS.

The methods available are—

I. Neutralisation of the required acid by the oxide, hydroxide or carbonate of the required metal.

This method is the one most generally applicable.

If the base used is alkaline, litmus paper may be used as indicator. If the base is insoluble in water, add the base to the acid till no more will dissolve, and either filter from the excess of base, or else carefully add sufficient acid to the solution to dissolve it.

It is worthy of note that with such bases it is often advantageous to have the acid present in slight excess.

Points worthy of notice regarding this method of preparing salts are:—

(*a*) The normal alkali (sodium, potassium, ammonium) salts of weak acids are alkaline to litmus, *e.g.* sodium phosphate (Na_3PO_4) is strongly alkaline to litmus; sodium hydrogen phosphate (Na_2HPO_4) is neutral, whilst sodium di-hydrogen phosphate (NaH_2PO_4) is acid. The potassium and ammonium phosphates show similar properties.

(*b*) Sodium sulphite (Na_2SO_3) is alkaline, and sodium bisulphite ($NaHSO_3$) is acid. Here there is no sharp neutralisation point, so other methods for their preparation have to be adopted. [See "Acid salts."]

(*c*) Some salts, such as lead nitrate, barium nitrate, barium chloride, etc., are of very limited solubility when in the presence of their own acid. Hence in the preparation of such salts, the acid used must be *dilute* (not more than two

normal) or an insoluble coating of the salt will form on the particles of the base, and prevent complete action. This is especially the case when preparing lead nitrate from litharge and dilute nitric acid. The ordinary bench acid (four normal) will be found too strong, and must be diluted with an equal volume of water.

(*d*) In the case of neutral ammonium salts, an indicator is not necessary. It is much quicker to add ammonia to the required acid till the solution just smells permanently of ammonia, and then to boil off the excess of ammonia. This will always take place during the boiling down necessary for crystallisation.

The following salts should be prepared by Method I.—

Potassium nitrate, sodium sulphate ($Na_2SO_4,10H_2O$), ammonium oxalate, ammonium nitrate, barium chloride, lead nitrate, magnesium sulphate, copper sulphate, copper nitrate, sodium hydrogen phosphate ($Na_2HPO_4,12H_2O_1$). [Average time required, 20 minutes per salt.]

II. The direct action of the acid on the metal.

This is of limited application. It may be used in the case of zinc and iron with *dilute* hydrochloric or sulphuric acids.

The metal is added to the acid in excess in the case of zinc, till no more will dissolve, the solution being kept hot. It is filtered and crystallised in the usual way.

Ferrous salts are dealt with below, as offering slight difficulty in preparing pure.

Method II may also be used with most nitrates, the same point being noted with regard to lead nitrate as in Method I.

By this method the following salts should be prepared—
Zinc sulphate, lead nitrate, copper nitrate.

Two special cases.

Ferrous sulphate, $FeSO_4, 7H_2O$.

Since ferrous salts are *very readily* oxidised by atmospheric air when in hot solution, a solution of ferrous sulphate cannot be boiled down to crystallisation. It must, therefore, be made by dissolving iron in hot dilute sulphuric acid of such a strength that the hot solution of ferrous sulphate so formed will crystallise *at once* on cooling. Hence proceed thus—

Half fill a large evaporating basin with dilute sulphuric acid of a strength about 1 vol. of pure acid : 6 vols. water. Warm on a gauze, and add iron filings *gradually* with constant stirring, till present in excess. Just before the action ceases, raise to a boil, and at once filter off, through a large funnel kept hot in the funnel heater, into a clean porcelain basin.

Cover up and set aside to crystallise. Drain and dry the crystals in the usual way.

Copper sulphate, $CuSO_4, 5H_2O$.—This may readily be prepared by the action of hot *strong* sulphuric acid on copper. The residues from the preparation of SO_2 may be used for this purpose.

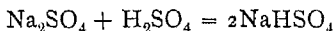
Allow the mixture to get quite cold. The copper sulphate will be deposited in the form of its monohydrate, $CuSO_4, H_2O$. Decant as completely as possible, and dissolve the dirty looking residue in as little hot water as possible, filter, and crystallise rapidly. Recrystallise the product once more in the usual way.

N.B.—If you are supplied with one salt of a metal and you are required to prepare another salt of the same metal from it, both salts being soluble in water, the method is to precipitate the carbonate of the metal by means of sodium carbonate solution (see p. 10), and after filtering and

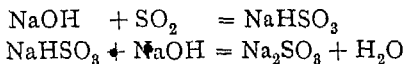
washing, to dissolve it in the usual way in the required acid.

(C) PREPARATION OF ACID SALTS.

These are generally prepared by first forming the neutral salt and then adding another equivalent (or the required amount) of the acid. *E.g.* sodium and potassium bisulphates ($NaHSO_4$ and $KHSO_4$) are made by half neutralising dilute sulphuric acid by soda and potash respectively. This is obviously done by taking two equal volumes (say two boiling tubes full) of dilute sulphuric acid, neutralising one with the required alkali, and adding the other volume of acid. The whole is then crystallised in the usual way.

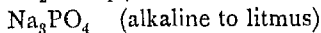
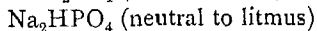
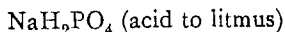
$$Na_2SO_4 + H_2SO_4 = 2NaHSO_4$$

In some cases, where the neutral point is not sharp to indicators (*e.g.* with carbonic or sulphurous acid), the acid salt is made by saturating a very strong solution of the alkali (soda or potash) with the acid (CO_2 or SO_2 *gas* in the above case) and cooling. The required salt crystallises out.

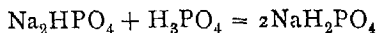
Note also that by first making the acid salt, in this way, the indicator difficulty when making the *normal* salt of such an acid is overcome. *E.g.* to make normal sodium sulphite (Na_2SO_3) two equal volumes of the same soda solution are taken, one is saturated with sulphur dioxide, giving $NaHSO_3$, and the other volume of caustic soda is then added.

$$NaOH + SO_2 = NaHSO_3$$
$$NaHSO_3 + NaOH = Na_2SO_3 + H_2O$$

Similarly for sodium carbonate, etc.

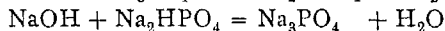
In the case of phosphoric acid, which is a tribasic acid, we proceed thus :—

The three possible sodium salts are—

NaH_2PO_4 (acid to litmus)
Na_2HPO_4 (neutral to litmus)
Na_3PO_4 (alkaline to litmus)

To make NaH_2PO_4, therefore, we must take two *equal* amounts of the acid, and neutralise one with NaOH (using litmus). This will give us Na_2HPO_4. Add the other amount of acid to it. Then—

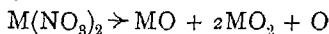
$$Na_2HPO_4 + H_3PO_4 = 2NaH_2PO_4$$

To make Na_3PO_4, we must take three equal volumes of soda solution; add two together and neutralise with phosphoric acid, giving Na_2HPO_4 as above. To this add the other volume of soda and crystallise.

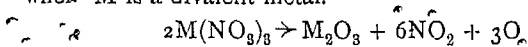
The following equations will make this clear—

$$2NaOH + H_3PO_4 = Na_2HPO_4 + 2H_2O$$
$$NaOH + Na_2HPO_4 = Na_3PO_4 + H_2O$$

(D) METALLIC OXIDES.

The ordinary basic oxide of a metal (*i. e.* the one usually formed when the metal burns in air) can be made from the metal by two methods which apply almost universally.

(i) **By first obtaining the nitrate (treat the metal with nitric acid diluted with its own volume of water), evaporating to dryness (sand-bath), and then igniting the nitrate strongly.**

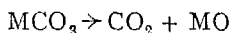
$$M(NO_3)_2 \rightarrow MO + 2MO_2 + O$$

where M is a divalent metal.

$$2M(NO_3)_3 \rightarrow M_2O_3 + 6NO_2 + 3O$$

where M is a trivalent metal.*

* In the case of nickel and cobalt, Ni_2O_3 and Co_2O_3 are left if the ignition is carried out carefully.

Even mercuric oxide can be made in this way, the ignition of the nitrate being done cautiously with addition of a little mercury. In many cases it is advantageous to extract the resulting oxide with boiling water, to remove any undecomposed nitrate.

In a few cases the carbonate is the better salt to employ—

$$MCO_3 \rightarrow CO_2 + MO$$

e.g. this would be used in the cases of lead, magnesium or zinc, although the nitrate method will work here.

To prepare the oxides of barium, strontium, and calcium, the nitrate method is not very serviceable, the temperature required being very high, especially in the cases of barium. The carbonate method offers the same difficulty. Hence we employ the special method of mixing the carbonate intimately with the required amount of carbon (lamp-black) and igniting strongly.

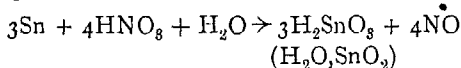
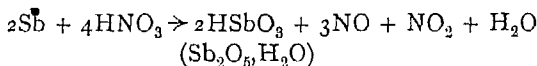
$$BaCO_3 + C = BaO + 2CO$$

The nitrate method fails in the case of aluminium, which is acted on by nitric acid only with difficulty.

In the cases of tin and antimony, the action of *strong* nitric acid is to give us metastannic and metantimonic acids respectively:—

$$3Sn + 4HNO_3 + H_2O \rightarrow \underset{(H_2O,SnO_2)}{3H_2SnO_3} + 4NO$$

and—

$$2Sb + 4HNO_3 \rightarrow \underset{(Sb_2O_5,H_2O)}{2HSbO_3} + 3NO + NO_2 + H_2O$$

The stannic acid is turned into stannic oxide (SnO_2) by filtering, washing thoroughly with boiling water, drying, and igniting strongly.

The antimonic acid, after washing and drying, must not

be heated above about 280° C. or the pentoxide required (Sb_2O_5) will give off oxygen and go to Sb_2O_4, the tetroxide.

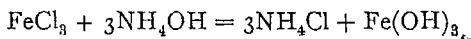
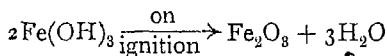
(ii) By adding caustic soda solution to a solution of the metallic salt, and igniting the washed and dried hydroxide thus prepared.

The oxides of barium, strontium and calcium *may* be thus prepared, but not advantageously, as they filter with difficulty.

In a few cases, ammonia is advantageously used instead of soda. These cases are with ferric iron, chromium, and aluminium salts. In each of these cases it is far better first to add ammonium chloride, as the precipitate separates much better.

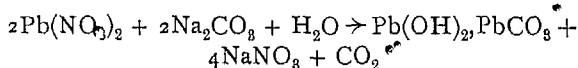
$$FeCl_3 + 3NH_4OH = 3NH_4Cl + Fe(OH)_3$$

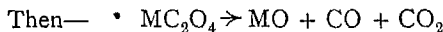
and—

$$2Fe(OH)_3 \xrightarrow[\text{ignition}]{\text{on}} Fe_2O_3 + 3H_2O$$

Similarly with chromium and aluminium.

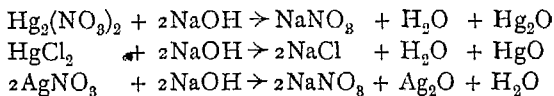
In any case, avoid much excess of alkali, as caustic soda is very difficult to wash completely out of a precipitate.

The hydroxides of chromium, aluminium, stannic and stannous tin, lead and zinc are all soluble in excess of caustic soda. In the case of the first three, ammonia is used. In the last two cases precipitation is very incomplete when ammonia is used (see under each metal in Part II); hence we precipitate the *carbonates* by adding sodium carbonate solution. Carbonates or basic carbonates are precipitated which readily, on ignition, leave the required oxide, *e.g.*—

$$2Pb(NO_3)_2 + 2Na_2CO_3 + H_2O \rightarrow Pb(OH)_2,PbCO_3 + 4NaNO_3 + CO_2$$

This caustic soda method fails entirely with stannous, ferrous, and manganous oxides (SnO, FeO, MnO). These oxides *very readily* take up oxygen from the air, forming SnO_2, Fe_3O_4 and Mn_3O_4. The only practicable way of preparing these oxides is to precipitate the oxalates by adding the calculated amount of potassium oxalate to the stannous, ferrous, or manganous solutions, to filter, wash and dry this oxalate, and to heat it gently in a combustion tube in a current of some neutral gas such as carbon dioxide.

Then— $MC_2O_4 \rightarrow MO + CO + CO_2$

Cool in the current of dioxide, and seal up at once when cold.

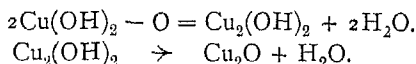
With caustic soda, solutions of mercurous, mercuric, and silver salts give the *oxide* at once, the hydroxides of these metals being unknown.

$$Hg_2(NO_3)_2 + 2NaOH \rightarrow NaNO_3 + H_2O + Hg_2O$$
$$HgCl_2 + 2NaOH \rightarrow 2NaCl + H_2O + HgO$$
$$2AgNO_3 + 2NaOH \rightarrow 2NaNO_3 + Ag_2O + H_2O$$

Cupric salts treated with caustic soda give cupric hydroxide $Cu(OH)_2$, which turns black on boiling, becoming partially dehydrated at that temperature even when suspended in the solution. Similarly, cuprous hydroxide, $Cu_2(OH)_2$ [obtained as a bright orange-coloured precipitate when cuprous salts, even though insoluble, are warmed with caustic soda], is partially dehydrated on boiling.

One special case deserves attention, viz. the preparation of cuprous oxide, Cu_2O. This is generally done by the gentle reduction of cupric oxide [in the form of $Cu(OH)_2$] dissolved in a suitable solvent. Many organic substances containing several alcoholic hydroxyl groups in the molecule will dissolve cupric hydroxide, forming a deep blue

solution. Glucose, or grape sugar, will do this, and at the same time will perform the function of the necessary mild reducing agent, a molecule of glucose taking up an atom of oxygen [forming gluconic acid].

Make a strong solution of copper sulphate, and to it add a 10 per cent. solution of glucose, employing about three quarters as many grams of glucose as of copper sulphate crystals. Sodium hydroxide is added with stirring till present in excess ($CuSO_4,5H_2O$ require $2NaOH$). The copper hydroxide first precipitated dissolves in the glucose solution with a fine blue colour. On now gently heating the solution, reduction takes place thus—

$$2Cu(OH)_2 - O = Cu_2(OH)_2 + 2H_2O.$$
$$Cu_2(OH)_2 \rightarrow Cu_2O + H_2O.$$

The heating is continued till there is no trace of blue or green in the solution. If it remains blue in spite of heating, it means insufficient soda has been added. The precipitated cuprous oxide is filtered, washed with boiling water, and dried in the steam oven.

N.B.—*Fehling's solution* is a solution of cupric hydroxide in alkali tartrate solution, being similar in nature to the above solution in glucose, before heating it. The tartrate, however, will not reduce it to the cuprous state, and hence the use of Fehling's solution to test whether a substance is a reducing agent or not.

It is important to remember that sodium hydroxide solution affords us a simple method of identifying many bases (if only one is present), as many metallic hydroxides are very characteristic. These are:—

Cuprous hydroxide, $Cu_2(OH)_2$ — Orange-coloured. Insoluble in excess of soda.

Cupric hydroxide, $Cu(OH)_2$	Blue-coloured. Insoluble in excess of soda.
Ferrous hydroxide, $Fe(OH)_2$	As precipitated is a dirty green. Insoluble in excess of soda. It rapidly absorbs oxygen from the air, and darkens in colour, becoming black, and then brown, passing into the ferric state.
Ferric hydroxide, $Fe(OH)_3$	Reddish-brown. Insoluble in excess of soda.
Manganous hydroxide, $Mn(OH)_2$	White. Insoluble in excess of soda. This precipitate rapidly darkens in colour, becoming finally almost black, due to absorption of atmospheric oxygen to form $MnO(OH)_2$, which is hydrated manganese dioxide.
Nickel hydroxide, $Ni(OH)_2$	Apple-green. Insoluble in excess of soda.
Cobalt hydroxide, $Co(OH)_2$	Dirty pink. The *blue* precipitate obtained when caustic soda is first added to a cobaltous salt is well known as a basic salt, *e.g.*—

$$Co(NO_3)_2 + NaOH = NaNO_3 + Co\begin{cases} OH \\ NO_3 \end{cases}$$

Mercurous oxide,	Hg_2O	Black.	The hydroxides are unknown.
Mercuric ,,	HgO	Yellow.	
Silver ,,	Ag_2O	Dark brown.	

Chromic hydroxide, $Cr(OH)_3$ — Greenish. Is soluble in excess of soda to a green solution.

The hydroxides of bismuth [$Bi(OH)_3$], magnesium [$Mg(OH)_2$] and cadmium [$Cd(OH)_2$] are white and insoluble in excess of soda. The hydroxides of lead, tin (stannous and stannic), aluminium and zinc are white and soluble in excess of soda to give colourless solutions.

(E) PREPARATION OF ACIDS FROM THEIR SALTS.

The general method is by treating the salt of the required acid with a stronger acid. The actual procedure must be modified to suit the particular acid which is being prepared.

E. g. *Hydrofluoric* and *hydrochloric* acids are gases prepared by the action of strong sulphuric acid on calcium fluoride and sodium chloride respectively. The former (HF) must not be prepared in glass apparatus, which it rapidly attacks. A platinum or lead retort is necessary, and a copper receiver, the gas being dissolved in water as it is evolved.

Nitric acid, being a volatile liquid, is made by distilling sodium or potassium nitrate with strong sulphuric acid.

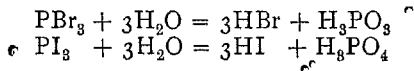
Phosphoric acid is a non-volatile soluble solid. For preparation see Part II under Phosphorus.

Chromic acid, CrO_3 (H_2CrO_4 known in solution only) is an exceedingly soluble crystalline solid.

Boric acid (HBO_2), crystalline solid, not very soluble.

Silicic acid (H_4SiO_4), gelatinous solid, practically insoluble.

Hydrobromic and *hydriodic* acids are got by special methods.

$$PBr_3 + 3H_2O = 3HBr + H_3PO_3$$
$$PI_3 + 3H_2O = 3HI + H_3PO_3$$

For particulars of the preparation of all these acids see any book on inorganic preparations.

(F) EXAMPLES OF THE PREPARATION OF SOME OF THE MORE IMPORTANT DOUBLE SALTS.

I.—The "Substituted Vitriols."

These are salts derived from the "vitriols," viz.—

Green vitriol, $FeSO_4,7H_2O$
White vitriol, $ZnSO_4,7H_2O$
Blue vitriol, $CuSO_4,5H_2O$ as usually met with, but $CuSO_4,7H_2O$ is known.

Magnesium sulphate, $MgSO_4,7H_2O$, manganous sulphate, $MnSO_4,7H_2O$, and the corresponding sulphates of nickel and cobalt are known also.

It is well known that when these salts are cautiously heated, all the molecules of water of crystallisation are driven off except one, which seems to be more firmly combined. This is seen best with ferrous sulphate; this last molecule of water of crystallisation cannot be driven off without the whole molecule decomposing. [See "Nordhausen" sulphuric acid in any text-book of Inorganic Chemistry.]

This molecule is known as *water of constitution*, and it is found that it can be replaced by a molecule of any alkali sulphate. *E.g.* $FeSO_4,(NH_4)_2SO_4,6H_2O$ is a well-known example. This replacement of the molecule of water by a molecule of alkali sulphate gives the salts so formed the name "*substituted vitriols*."

The series will then have the formula $M''SO_4,M'_2SO_4,6H_2O$ where M'' is any of the divalent metals Fe, Ni, Co, Zn, Mg, Mn, Cu, and M' is any of the alkali metals

Na, K, etc., or NH_4. Practically the whole series is known, and they afford examples of some of the most beautifully crystallised salts we can make.

Examples of the preparations are given below.

(*a*) FERROUS AMMONIUM SULPHATE, $FeSO_4, (NH_4)_2SO_4, 6H_2O$.

Start from iron filings, H_2SO_4, and NH_4OH solution. Noting from the formula that we have equal amounts of SO_4 combined with Fe and with $(NH_4)_2$, we measure out two equal volumes of sulphuric acid (1 : 5), say two boiling tubes full, into two separate basins. One is neutralised with ammonia (see above), and the other with iron filings (see preparation of ferrous sulphate).

They are filtered *hot* through separate funnels into a large basin, and set aside to crystallise.

N.B.—The solutions must be of such a strength whilst hot that on cooling they crystallise without any boiling down, or the ferrous salt will be spoilt.

Examine the crystals under a microscope and note their shape. Compare with the shapes of crystals of the other substituted vitriols. (¾ hr.)

(*b*) COPPER POTASSIUM SULPHATE, $CuSO_4, K_2SO_4, 6H_2O$.

Prepare on similar lines to the above, starting from copper *oxide*, however.

N.B.—Avoid having the potassium sulphate solution alkaline, through neutralising with too much potash. It will be better to err on the acid side. If the least excess of potash is present, on mixing the solutions we shall get a gelatinous blue precipitate of copper hydroxide, very difficult to filter. (¾ hr.)

(*c*) NICKEL AMMONIUM SULPHATE, $NiSO_4, (NH_4)_2SO_4, 6H_2O$ is a very beautiful salt.

Prepare as above, starting from nickel carbonate. (¾ hr.)

(*d*) ZINC POTASSIUM SULPHATE, $ZnSO_4, K_2SO_4, 6H_2O$. Start from granulated zinc. (1 hr.)

(*e*) MANGANOUS AMMONIUM SULPHATE, $MnSO_4, (NH_4)_2SO_4, 6H_2O$, is an extremely pretty salt, when well crystallised. In this case start straight away from manganous sulphate and ammonium sulphate, by weighing out molecular proportions, dissolving, mixing, filtering and crystallising. [$MnSO_4, 4H_2O$ is the hydrate of $MnSO_4$ usually met with.] If the solution is allowed to crystallise very slowly (by evaporating till the solution is just saturated when cold and then setting aside for a week or two), very beautiful crystals are obtained. ($\frac{3}{4}$ hr.)

II.—The Alums.

These beautiful salts have the general formula $R'''_2(SO_4)_3, R'_2SO_4, 24H_2O$, where R''' is any of the trivalent metals Fe''', Al, Cr, and R' is any of the alkali metals or (NH_4).

R''' may also be Mn''', but these alums are very difficult of preparation. Also the potassium and ammonium alums crystallise the best. Do not attempt to prepare sodium alums. The crystals of all alums are regular octahedra.

Three alums may be prepared, illustrating two general methods and one special method.

(*a*) *Aluminium ammonium alum*, $Al_2(SO_4)_3, (NH_4)_2SO_4, 24H_2O$.

Weigh out molecular proportions of aluminium sulphate, $Al_2(SO_4)_3, 18H_2O$, and ammonium sulphate $(NH_4)_2SO_4$. Dissolve in distilled water, filter if necessary, and mix. Allow to crystallise slowly. Large well-shaped crystals may easily be grown. ($\frac{1}{2}$ hr.)

(*b*) *Iron ammonium alum*, $Fe_2(SO_4)_3, (NH_4)_2SO_4, 24H_2O$. Starting from iron sesquioxide ammonia and dilute sulphuric acid, prepare this salt by a method similar to

that given for the preparation of ferrous ammonium sulphate.

Note that three times as much sulphuric acid is neutralised by iron as by ammonium. (1¼ hrs.)

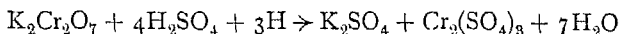
EXERCISE.

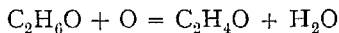
This should be varied by starting from Ferrous sulphate, $FeSO_4$, $7H_2O$. This is oxidised to ferric sulphate by adding to the solution the right amount of strong sulphuric acid, warming, and *carefully* adding concentrated nitric acid. The excess of nitric acid *must* be evaporated off by taking down nearly to dryness on a *water-bath*, and redissolving in water. The calculated amount of ammonium sulphate is then added, and the whole crystallised slowly. Very perfect crystals are readily obtained. (Several hours required for this.)

If you cannot see how to do these two experiments properly, see appendix.

(*c*) *Chrome alum*, $Cr_2(SO_4)_3,K_2SO_4,24H_2O$.

The starting-point for this alum is potassium bichromate, $K_2Cr_2O_7$. Note that if reduced to sulphates, by adding sulphuric acid and a reducing agent, it will form potassium and chromium sulphates in the right proportions to form the alum. [Potassium bichromate has no water of crystallisation.]

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

The most suitable reducing agent to use is alcohol (methylated spirits). It is oxidised to aldehyde thus—

$$C_2H_6O + O = C_2H_4O + H_2O$$

One molecule of alcohol can thus supply two atoms of hydrogen.

Calculate the amounts of each required, on the assumption that pure concentrated sulphuric acid is 95 per cent. H_2SO_4, and methylated spirits 80 per cent. C_2H_6O. Make a *strong* solution of the bichromate in water, add the sulphuric cautiously, cool to 0°C., and add the alcohol carefully.

Reduction is complete when the solution is a pure emerald-green, with no trace of yellow about it. Stand overnight. Next morning filter off on the pump the violet powder that crystallises out, and wash twice, *as quickly as possible*, with ice-water.

Then dissolve in the *least possible* amount of water at about 40–45°C. (not above), and set aside to crystallise slowly.

N.B.—If the temperature of the solution gets much above 40°, a sticky non-crystalline variety is liable to be formed, and the preparation will be useless.

Experiment—

Mix a saturated solution of aluminium alum with about one-eighth of its volume of a saturated solution of chrome alum, and set the mixture to crystallise.

Describe the crystals. Do they not look like iron alum? How would you distinguish them from iron alum crystals *without* analysing them?

Leave a crystal of chrome alum in a saturated solution of aluminium alum. Describe and explain what you see happening.

(G) PREPARATION OF INSOLUBLE SALTS BY PRECIPITATION.

When an insoluble salt is being prepared by the method of double decomposition, it will often be found advisable to precipitate with *both solutions boiling*, and to add the precipitant gradually. *Do not have the solutions too strong.*

This method of gradual precipitation at a boiling temperature is *absolutely necessary* in the case of barium and strontium salts such as barium chromate ($BaCrO_4$), barium sulphate ($BaSO_4$), etc., and also in the case of calcium oxalate (CaC_2O_4), otherwise the precipitates will be so fine as to pass through the filter-paper. In most cases it will

be found that a better precipitate is obtained from hot solution than from cold.

Exceptions are the carbonates of metals (other than barium, strontium and calcium) and lead chromate.

These are generally made in the cold. Insoluble mercury salts are best precipitated cold, or basic salts may be obtained instead of the one required.

Prepare the following salts by this method—

(i) *Lead chloride*, starting from litharge or white lead. This salt is *soluble* in boiling water, from which it may be recrystallised.

N.B.—Do NOT try to make this salt by dissolving litharge or lead carbonate in dilute hydrochloric acid. Why?

(ii) *Lead bromide* (soluble in hot water) and *lead iodide* (do.) starting from lead acetate and potassium bromide or iodide. If the filtered precipitate be dissolved in the necessary quantity of boiling water, and set aside to crystallise slowly, very beautiful preparations result.

(iii) *Barium chromate* from barium chloride and potassium chromate. To be done with *both* solutions boiling.

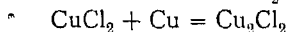
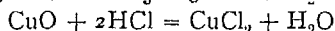
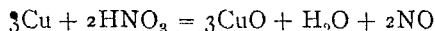
N.B.—If potassium bichromate is used, see under Barium, Problem 2, and under Chromium, Problem 10.

(iv) Calcium oxalate, starting from calcite or marble ($CaCO_3$) and ammonium oxalate $(NH_4)_2C_2O_4,H_2O$.

N.B.—The following special case deserves notice, viz. the preparation of cuprous chloride, Cu_2Cl_2. We cannot make this by double decomposition in the ordinary way, because cuprous salts are all insoluble in water. Hence also the solution of cuprous oxide in dilute hydrochloric acid is not available. But cuprous chloride is soluble in hot strong hydrochloric acid, forming the complex acid $H_4Cu_2Cl_6$ (*i.e.* $Cu_2Cl_2 + 4HCl$). On diluting with water this is dissociated and the required cuprous chloride is precipitated.

Cuprous oxide, however, is comparatively expensive, so that if we can start from either copper or cupric oxide, it will be far better to do so. Now cupric chloride is *reduced* to cuprous chloride by copper in the presence of strong hydrochloric acid, and the cuprous chloride so formed dissolves in the excess of acid. $Cu + CuCl_2 = Cu_2Cl_2$.

Hence dissolve cupric oxide in considerable excess of hot strong hydrochloric acid, add rather more than another equivalent amount of copper turnings, and boil gently till the solution goes clear. *Or* starting from *copper*, add to the mixture of copper and strong hydrochloric acid sufficient strong nitric acid to convert rather less than one-half of the copper to the oxide.

$$3Cu + 2HNO_3 = 3CuO + H_2O + 2NO$$
$$CuO + 2HCl = CuCl_2 + H_2O$$
$$CuCl_2 + Cu = Cu_2Cl_2$$

which then dissolves in the excess of hydrochloric acid. $Cu_2Cl_2 + 4HCl = H_4Cu_2Cl_6$. In each case, the weights of the ingredients to be taken should be calculated. Take pure concentrated hydrochloric acid as 30 per cent. HCl, and nitric acid as 60 per cent. HNO_3.

In *either* case, when the reduction of the cupric chloride is complete, pour the whole into a gas-jar or very large beaker of cold water. Allow the white precipitate of cuprous oxide to settle, syphon off the liquid, wash two or three times with dilute sulphurous acid solution by decantation, and then transfer as quickly as possible to the filter-pump, wash once with sulphurous acid, and four times with as little glacial acetic acid as possible. This last is to get rid of sulphurous acid, which would oxidise to sulphuric, and spoil the preparation. Then transfer the substance just as it is to a clock-glass, which is placed over a vessel of boiling

water. In about 15 to 20 minutes the preparation will be perfectly dry, without any trace of oxidation, and should be bottled at once. The washing with sulphurous acid is to prevent oxidation by atmospheric oxygen to a basic cupric salt, Cu_2OCl_2.

See also Problem 5 under Copper.

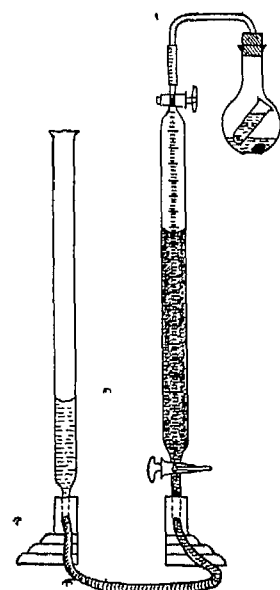
NOTE ON DETERMINATION OF EQUIVALENTS.

There are in general three methods of finding the equivalents of elements.

A. The determination of the weight of the element required to displace 1 gram of hydrogen from acids, etc.

The equivalents of magnesium, zinc, cadmium, iron (ferrous), tin(-ous), aluminium and calcium can be found in this way.

FIG. 1.

The apparatus used may be a simple form of "nitrometer" tube, such as that shown in Fig. 1 (which is an ordinary gas-burette). There are also numerous simple modifications which may be left to the student's own ingenuity.

The well-known "syphon-bottle" apparatus may also be used, and, *with all necessary precautions and corrections*, will be found to give *excellent* results.

The great advantages of the syphon-bottle method are—

(*a*) That a comparatively large volume of gas may be measured, and the percentage error of reading thus reduced.

(*b*) Heat may be applied, which is necessary in the cases of iron, tin and aluminium. Subsequent cooling under the tap is easy.

The full description of the syphon-bottle method is given here, with all necessary precautions.

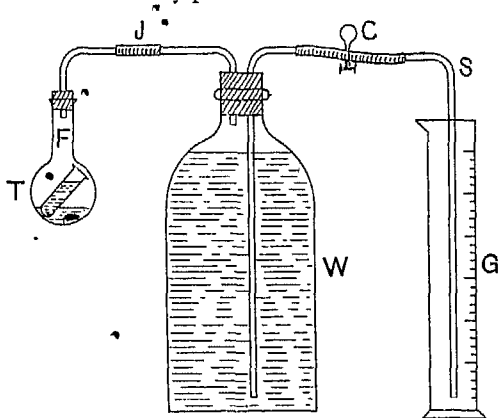



FIG. 2.

All stoppers must be rubber, and must be wet. **W** is a winchester bottle fitted as shown. **F** is a small flask containing a test-tube of as large dimensions as permissible, which should fit exactly in the position shown. The required acid is put in this tube, and water, if necessary, in the flask. The syphon tube **S** is now filled with water by opening the clip **C** and blowing into the other tube at **J**. (*N.B.*—This is because, at the end of the experiment, the tube **S** is full of water. Hence it must also be full to start with, for obvious reasons.) A weighed amount of the metal whose equivalent

is required is now dropped into the flask, and the connection at **S** having been made, the flask is put into position on the cork. When the cork is forced in, a slight increase of pressure will be caused inside the apparatus. This is allowed for by putting a boiling tube half full of water under **S**, and raising it (with the end of **S** under the water) till the levels of water inside the bottle **W** and in the boiling tube are the same. The clip **C** is opened for a few moments and the pressure inside falls to atmospheric. **C** is then closed. (*N.B.*—If the water-level in the boiling tube is *below* that in the bottle, the syphonic action will cause the pressure inside to fall *below* atmospheric, and *vice versa.*) The boiling tube is removed, a graduated cylinder **G** is put into position, **C** is opened, and **F** tipped up so that the acid gets to the metal. If necessary, heat is applied to the acid, using a wire gauze, and after solution is complete. The whole apparatus is cooled under the tap with **C** open and **S** well under the water in **G**. Lastly, equalise the pressure inside and outside the apparatus by raising or lowering **G** before closing the clip. Then read the volume of water in **G**. This is obviously the volume of gas evolved. Correct for pressure, temperature, and pressure of aqueous vapour. If these directions are carefully followed, surprisingly accurate results will be obtained.

N.B.—The equivalent of aluminium by this method is most easily carried out by using caustic soda solution instead of acid. The results, however, are not quite so good. But strong hydrochloric acid reacts *fairly* readily with aluminium.

Use dilute sulphuric acid for magnesium, zinc and cadmium; dilute hydrochloric for calcium and iron (hot for the latter), and fairly strong hydrochloric acid, also hot, for tin and aluminium.

B. The determination of the percentage composition of the oxide.

This is done either by synthesis of the oxide, *via* the nitrate, from a known weight of metal, or analysis of the oxide by reduction in hydrogen.

By synthesis of the oxide the equivalents of magnesium, zinc, copper(*-ic*), lead, antimony (nitric acid forms Sb_2O_5 giving the *-ic* equivalent), tin (nitric acid forms SnO_2 giving the stann*ic* equivalent), cadmium and ferric iron. The procedure is to treat a weighed quantity (1–2 grams) of the metal with the minimum of strong nitric acid necessary to effect solution. The liquid is then carefully evaporated dry and the residue ignited, cautiously at first. The experiment may be carried out either in a 35-c.c. hard-glass flask, or in a porcelain basin or large crucible.

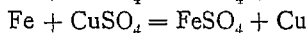
By the reduction of the oxide can be found the equivalents of cuprous and cupric copper, lead (di- and tetravalent), nickel and cobalt.

N.B.—When reducing lead peroxide (PbO_2) in hydrogen, convert it into litharge before the stream of hydrogen is started, or an explosion will result, as oxygen is freely evolved from lead peroxide before the temperature necessary for reduction to lead is reached.

The equivalents of non-metals can sometimes be found by direct synthesis of the oxide, *e.g.* carbon, sulphur, silicon. Special precautions to prevent loss of oxide will be necessary, which will differ with the volatility, etc., of the oxide.

C. The replacement of one substance by another.

Examples—

$$Zn + CuSO_4 = ZnSO_4 + Cu$$
$$Fe + CuSO_4 = FeSO_4 + Cu$$

equivalent of the other can be found. Similarly with iron. Silver also is readily replaced from silver nitrate by zinc or magnesium.

D. The analysis of the chloride or bromide of the substance.

This is done by precipitation of the halogen as silver chloride or bromide, and weighing the precipitate. For details see any book on Quantitative Analysis.

If the chloride is soluble in water, we may find the percentage composition by titration with $\frac{N}{10}$ silver nitrate (*q.v.* under Volumetric Problems, pp. 100–1).

PART II

PROBLEMS

QUALITATIVE AND QUANTITATIVE

HYDROGEN. H = 1·01 (O = 16).

Equivalent = 1·01. *Atom, monovalent; being taken as the unit of valency and of equivalents.*

ABSOLUTELY pure hydrogen can only be obtained by the electrolysis of barium hydroxide solution, as in every other case impurities in the shape of reduction products of the electrolyte are introduced; *e.g.* electrolysis of dilute sulphuric acid introduces sulphur dioxide and hydrogen sulphide. Electrolysis of caustic soda introduces slight traces of hydrocarbons due to reduction of the sodium carbonate from which it is impossible to free the hydroxide.

In the case of barium hydrate, any carbon dioxide absorbed is precipitated out of the sphere of action as barium carbonate.

Reducing power of electrolytic hydrogen.

1. Set up an apparatus for the electrolysis of dilute sulphuric acid. Make the following substances in turn the cathode, and notice whether the hydrogen has any reducing action on it: arsenic, antimony, bismuth, (palladium), lead dioxide, lead sulphate. (The two latter may be pasted on to a lead plate and allowed to dry.)

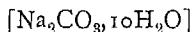
2. Devise a simple chemical method for finding the vapour density of hydrogen. ($1\frac{3}{4}$ hrs.)

A few problems on WATER.

3. Set up a simple apparatus to find the percentage composition of water by weight. Dumas' method to be used. (2 hrs.)

4. You are given a salt of the following composition—

Anhydrous substance . . .	37·1 %
Water of crystallisation .	62·9 %
	100·0 %

[$Na_2CO_3, 10H_2O$]

You are required to find the difference in the *heats of solution of comparable quantities* of the hydrated and anhydrous salts. Calculate the amount of heat evolved or absorbed (which?) by the heat of solution of 1 gram of water of crystallisation. Confirm by experiment with other crystalline salts, *e.g.* $CuSO_4, 5H_2O$.

N.B.—Use a delicate thermometer, reading to ·1° C. at least. Also it will be necessary to employ some method of correction for loss of heat by radiation, as the solution of the substance may require some time.

If the solution is fairly dilute, its specific heat may be taken as 1, but it will be better to find the *specific heat of the dissolved substance* by any of the well-known methods. (*e.g.* diluting a solution of known composition with a known weight of hot water).

Query—Does the heat of solution of 1 gram of water of crystallisation approximate to any well-known physical constant for water? To what might you expect it to approximate?

5. You are supplied with hydrated and with anhydrous sodium carbonate ($Na_2CO_3, 10H_2O$ and Na_2CO_3). Find the density of each substance, and hence—

(*a*) Find the density of water of crystallisation.

(*b*) Find the molecular volume of the hydrated salt. Compare it with the volume of ice formed by the weight of water of crystallisation in the molecule. What do you notice? Confirm with some other substance that is easily dehydrated.

GROUP I—SODIUM, POTASSIUM, COPPER, SILVER.

SODIUM. Na = 23.

Equivalent = 23. *Atom therefore monovalent.*

1. Determine the equivalent of sodium by purifying some sodium chloride and determining the amount of chlorine in a weighed quantity by means of $\frac{N}{10}$ silver nitrate. Calculate the weight of sodium that combines with the equivalent weight of chlorine (35 5). For details see under $\frac{N}{10}$ Silver Nitrate, p. 100.

2. *Reducing power of sodium amalgam.*

Find whether sodium amalgam reduces potassium chlorate to potassium chloride in aqueous solution. If not, find whether reduction takes place when the sodium amalgam forms an electric element with the following metals: magnesium, zinc, iron, lead, copper, and mercury, using the potassium chlorate solution as the exciting liquid. An H-tube is suggested as a convenient form for the cell, as shown in the figure. **V** is a *delicate* voltmeter which must have a high resistance, as such a small cell will have a fairly high resistance. Draw a time-E.M.F. curve over about 10 minutes with each of the above metals, and note whether polarisation takes place. (The shape of the curve will show this.) Then short-circuit the cell for about 10 minutes, and compare the amounts of reduction that take place (round the

other metal, of course) by pipetting out the liquid from round this plate, adding a drop of phenol phthalein, neutralising exactly with $\frac{N}{10}$ nitric acid, and titrating with $\frac{N}{100}$ silver nitrate in the usual way.

Do you notice any connection between the amount of reduction that has taken place and the observed E.M.F. of

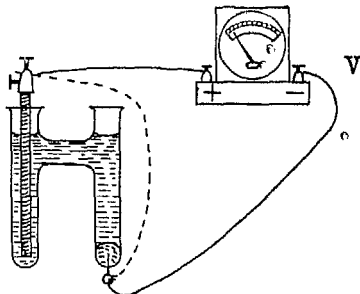



FIG. 3.

the element? Do you notice any connection between the amount of reduction and the amount of polarisation? What connection would you expect to notice? (3 hrs.)

3. See under Carbon, Problem 3.

POTASSIUM. K = 39·1.

Equivalent = 39·1. *Atom is therefore monovalent.*

1. Find the equivalent of potassium by carefully purifying some potassium chloride and estimating the chlorine in a weighed portion by titration with $\frac{N}{10}$ silver nitrate.

For details see Problem 2, under $\frac{N}{10}$ Silver Nitrate.

2. Find whether the following substances assist in the decomposition of potassium chlorate by heat, and compare

roughly their efficiency: ferric oxide (Fe_2O_3), precipitated silica (SiO_2), chromic oxide (Cr_2O_3). What obvious precautions must be taken in order that comparison may be made? Observe anything worthy of note, and explain the actions as far as possible. (1½ hrs.)

3. Compare the actions of potassium chlorate and potassium perchlorate solutions on ferrous sulphate solution containing excess of dilute sulphuric acid.

From your results, devise a scheme to (*a*) test for, (*b*) estimate, potassium perchlorate, chlorate, and chloride in the presence of each other.

COPPER. Cu = 63·6.

Equivalents { 31·8 (*in cupric compounds*).
63·6 (*in cuprous* ,,).

The atom of copper is probably divalent only, as the cuprous compounds appear to possess the double formulæ, e. g.

$$Cu_2Cl_2, \text{ i. e. } \begin{matrix} Cu—Cl \\ | \\ Cu—Cl \end{matrix} \qquad \textit{Compare mercury.}$$

1. (i) The equivalent of *cupric* copper may be found by the oxide method in several ways.

(*a*) By turning a weighed amount of copper to the oxide *via* the nitrate.

(*b*) By reducing the oxygen in pure hydrogen at red heat.

(*c*) By burning "spongy" copper or reduced copper to copper oxide, CuO, in a stream of oxygen, or simply by ignition in an open dish with stirring and a very free access of air. The equivalent should be found by at least two of the above methods.

(ii) The equivalent of *cuprous* copper may be found (*a*) by analysis of cuprous oxide, which must be of a reliable purity, and must not contain any of the hydroxide.

(*b*) An excellent method also is the direct synthesis of

cuprous sulphide (Cu_2S), by heating copper foil in sulphur vapour (crucible experiment). Remember that the sulphide readily burns in air, and must therefore be protected from the air whilst hot. Hydrogen does *not* reduce Cu_2S, but will reduce CuS to Cu_2S at red heat.

2. Compare the action of dilute hot sulphuric acid (1:6) on the two oxides of copper. Identify all products of the reaction in each case, and write equations to explain the actions. ($\frac{1}{2}$ hr.)

3. The above example may be extended somewhat, and the action of hot dilute sulphuric acid on red copper oxide confirmed quantitatively.

According to your equation, what relation exists between the amounts of copper left over and in the copper sulphate formed? Devise a simple experiment to confirm this. ($1\frac{3}{4}$ hrs.)

4. Devise a simple method of finding the action on metallic copper of—

(*a*) Pure strong hydrochloric acid (air-free).

(*b*) Ditto, but so that air has free access.

(*c*) Moist air-free hydrochloric acid gas.

(*d*) Moist hydrochloric acid gas and air.

5. Find the action of (*a*) dilute, (*b*) strong hydrochloric acid on the red oxide of copper. How does it differ from the action of sulphuric on the same oxide? ($\frac{3}{4}$ hr.)

6. To some copper sulphate solution add potassium iodide solution till no more precipitate falls. (Solutions should not be more than 5 to 10 per cent. in strength.) Filter, wash the precipitate with hot water, and identify both precipitate and filtrate.

N.B.—The precipitate may be treated with—

(*a*) Strong sulphuric acid, and warmed.

(*b*) Caustic soda solution, and warmed.

Hence write the equation for the action of potassium iodide on copper sulphate.

Now try it *quantitatively*, i. e. by adding together solutions containing weights of the substances proportional to their equivalents (*i. e.* $CuSO_4,5H_2O : 2KI$). Filter, and test the filtrate for (*a*) copper, (*b*) an iodide, (*c*) free iodine.

Again prepare exactly equivalent solutions of the two salts, but before mixing them, add some strong sulphurous acid solution to the copper sulphate. Then add the iodide till no more precipitate falls. (The solution should still smell of sulphur dioxide.)

Compare the amount of potassium iodide required to completely precipitate the copper with that required when no sulphur dioxide is present. Test the filtrate for—

(*a*) Copper. (*b*) An iodide.

(*c*) Free iodine.

Write equations and give full explanations.

7. Find the action of ammonium thiocyanate on copper sulphate solution by making equivalent solutions of each salt (*i. e.* $CuSO_4,5H_2O : 2NH_4CNS$) and mixing them by adding the thiocyanate to the copper salt till no more precipitate falls. Describe exactly what you see, and how the precipitate changes. After a minute or so, warm, and add gradually, whilst warming, some strong sulphurous acid.

Identify the precipitate by treating with—

(*a*) Caustic soda solution.

(*b*) Strong sulphuric acid, and warming.

Write equations. ($\frac{3}{4}$ hr.)

8. For a similar interesting and extremely important reaction of copper, see the action of copper sulphate with potassium cyanide. (*This must only be done according to very careful directions and under direct supervision, owing to the excessively poisonous gas given off.*) Thus—

In a small flask, fitted with a cork carrying a thistle tube and a delivery tube fitted with a jet for burning a combustible gas, put a solution of copper sulphate. In the neck put a plug of cotton wool (to "scrub" any gas evolved), put the cork in position, and put the flask in a good draught cupboard. Now add, through the thistle funnel, an *equivalent quantity* of potassium cyanide solution (*i. e.* 2KCN to every $CuSO_4,5H_2O$ taken.) Note *exactly* what happens. If no gas comes off, warm gently. When the gas comes off, apply a light to the jet (first allowing time for the air to be swept out of the flask). Note the flame. What is the gas? When the action is over, filter off the precipitate, wash thoroughly and find out what it is. Write equations. Note especially the action of more potassium cyanide solution on this precipitate. (1½ hrs.)

9. Find the action of heat on copper oxalate. Arrangements must be made to heat it *away from the air.* Identify both the residue and the gases evolved. (20 mins.)

(*N.B.*—Copper oxalate is not easy to prepare, owing to its being exceedingly difficult to filter.)

10. *On a separation of copper from cadmium.*

Find the action of sodium thiosulphate on copper sulphate solution by the following method—

Add sodium thiosulphate solution (freshly prepared) to copper sulphate solution in a small flask, standing on white paper, till the blue colour just disappears. The addition must be made rapidly, but avoid a great excess of thiosulphate. Now boil for five minutes, filter, and identify precipitate. Test the filtrate for copper.

Try a similar test with cadmium sulphate. From your results, devise a separation of copper from cadmium that can be used in Group II. (Qualitative Analysis). (¾ hr.)

11. Boil a solution of copper sulphate for a few minutes

with some animal charcoal. What happens? Any explanation? Burn some of the animal charcoal and analyse the ash. Does this explain the decolorisation of copper sulphate? (¾ hr.)

SILVER. Ag. = 108.

Equivalent = 108. *Atom therefore monovalent.*

1. Devise a method of finding the equivalent of silver. Remember that silver oxide (Ag_2O) is not very stable, and that it will not stand heating. The chloride or bromide are produced by direct combination, but *melt easily*. They are also reduced by heating in hydrogen. Also $AgNO_3$ + $HCl = AgCl + HNO_3$, which can be filtered, washed, dried and weighed readily.

2. *Action of a mixture of chromate and chloride on silver nitrate.*

To some potassium chromate solution add a *little* sodium chloride solution (1 or 2 cc. of $\frac{N}{10}$ NaCl). To this solution add $\frac{N}{10}$ silver nitrate solution dropwise. As soon as the last drop makes the precipitate appear pink, and remains so, filter. Add more silver nitrate solution to the filtrate. What do you think the precipitate is? Confirm your supposition. Also shake some up well with some common salt solution.

From these results explain the use of potassium chromate as an indicator in titrations with $\frac{N}{10}$ silver nitrate. (15 mins.)

3. *Some reactions of silver salts.*

(*a*) To a solution of silver nitrate add dropwise a solution of sodium sulphite till in excess. Note everything that happens, and try and write equations. Now boil the

solution, and find out what the precipitate is and whether anything is evolved (smell). What does the filtrate contain? Give equations.

(*b*) Prepare some silver sulphite by adding some sodium sulphite solution to some silver nitrate solution, avoiding excess. Wash thoroughly with *cold* water; transfer to a test-tube, add water, and boil. Is anything evolved? What is left? Filter, and see if any silver is left in the filtrate. If so, in what condition is it? Write equations, and compare the action of heat on silver sulphite with the action on the solution in (*a*). Explain these two actions, and give any parallel cases that you have come across.

(*c*) To a solution of silver nitrate, cold, add cold sodium thiosulphate gradually till in excess. Note what happens, and boil the solution so obtained. Identify precipitate and filtrate. Compare with (*a*) above. (1 hr.)

4. Find the action of ferrous sulphate solution (neutral) on silver nitrate solution. [*Use equal volumes of equimolecular solutions.*] Do not have the solutions too dilute. If no action in the cold, boil for some time. Identify both precipitate and filtrate. Try and write equations. Note whether or not any oxides of nitrogen appear to be given off. (20 mins.)

GROUP II.—MAGNESIUM, ZINC, CADMIUM, MERCURY, BARIUM, STRONTIUM, CALCIUM.

MAGNESIUM. Mg. = 24·3.

Equivalent (*one only*) = 12·15. *Atom divalent.*

1. Find the equivalent of magnesium by—

(*a*) The hydrogen method, using very dilute hydrochloric acid. The hydrogen is best measured in an ordinary gas-burette. Devise a suitable apparatus.

(*b*) The nitrate method. (1 hr. each.)

2. Compare the action of sodium carbonate solution on magnesium sulphate solution with that of sodium bicarbonate on the same substance (both in the cold). Do they both give normal magnesium carbonate, or is a basic carbonate produced? By what simple method can a basic carbonate be distinguished from a normal carbonate? (See also under Zinc and Copper.) (1 hr.)

3. *Investigation of some magnesium salts.*

To a solution of magnesium ammonium chloride (got by mixing solutions containing weights of each in the proportion of $MgCl_2 : 2NH_4Cl$) add sodium phosphate solution and ammonia. Shake thoroughly, filter off the precipitate, wash with dilute ammonia (examining a specimen under microscope meanwhile), and dry *thoroughly* at 100° C. Identify this precipitate by qualitative analysis. Prove its formula by heating some in a hard-glass tube, and finding (*a*) what is evolved, (*b*) *exactly* what is left. Write equations.

4. Repeat (3), using sodium arsenate instead of phosphate. Compare the precipitate under the microscope with the corresponding phosphate. Analyse the precipitate qualitatively as before, and find the action of (1) gentle, (2) strong heat on it, in a hard-glass test-tube. Does the action when heated strongly differ in any way from the action on the corresponding phosphate? How would you expect it to differ? Give equations.

5. Investigate the action of ammonium hydroxide on magnesium chloride or sulphate solution—

(*a*) Without the previous addition of ammonium chloride. Filter, identify the precipitate, and test the filtrate for magnesium by adding sodium phosphate.

(*b*) *First* adding ammonium chloride.

From your results state clearly why ammonium chloride is added to the solution before adding ammonia, in qualitative analysis, to precipitate Group III. A. (½ hr.) (See also under Zinc.)

6. To a solution of iodine in potassium iodide add potash till the colour has *almost gone.* Then add this to some magnesium sulphate solution. What do you think the precipitate is? Watch it for a few minutes. What is happening to it? If nothing happens, warm it gently. (5 mins.)

ZINC. Zn = 65·4.

Equivalent = 32·7. *Atom therefore divalent.*

1. Find the equivalent of zinc, using (*a*) the hydrogen method, (*b*) the oxide method. (1 hr. each.)

2. Compare the action of sodium carbonate (Na_2CO_3) solution with that of sodium bicarbonate ($NaHCO_3$) solution on zinc sulphate solution. Does either reagent produce zinc carbonate ($ZnCO_3$) or only a basic carbonate? (Compare magnesium, copper, etc.)

3. Treat zinc with cold, fairly dilute (1 : 4) nitric acid. Are any oxides of nitrogen given off? If so, which? Any other gas? If not, find out, by filtering and analysing the filtrate qualitatively (best after standing with the zinc overnight), what has become of the zinc and the oxides of nitrogen that ought to have come off.

4. Investigate the action of ammonium hydroxide on a zinc salt in solution—

(*a*) Without the previous addition of ammonium chloride. Filter, identify the precipitate, and test the filtrate for zinc. (How?)

(*b*) *First* adding ammonium chloride.

From your results state clearly why ammonium chloride

is added before ammonia in precipitating Group III. A in qualitative analysis. (20 mins.)

CADMIUM. Cd = 112·4.

Equivalent = 56·2. *Atom is therefore divalent.*

1. Find the equivalent of cadmium by the oxygen method. Confirm by the hydrogen method. (1 hr. each.)

2. As under Zinc. Is it possible to prepare the normal carbonate, $CdCO_3$? Find the action of heat on the product.

3. *On the separation of cadmium from copper.*

To a solution of a cadmium salt add potassium cyanide solution dropwise, till in excess. What do you notice? Try the action of the ordinary tests for cadmium on this solution, *e g.* caustic soda, ammonia, ammonium carbonate and hydrogen sulphide. Explain what you observe.

Compare your observations with those of a similar experiment with a COPPER salt. Hence explain the chemistry of the cyanide separation of copper from cadmium in Group II. ($\frac{1}{2}$ hr.)

4. Investigate the action of ammonia with and without the addition of ammonium chloride, as under Zinc, Problem 4. Is any difference noticeable? (20 mins.)

MERCURY. Hg = 200.

Equivalent = 200. *Atom is therefore divalent. Mercury also has an equivalent of* 100, *but it is doubtful whether the atom is monovalent, as the mercurous salts seem to have the double formula,* e. g. Hg_2Cl_2, *etc., being therefore*

$$\begin{array}{l} Hg\text{—}Cl \\ | \\ Hg\text{—}Cl. \end{array}$$

This is probably the case also with the cuprous salts, q v.

1. Determine the equivalent of divalent mercury by (1) estimating the oxygen in red mercuric oxide, HgO, by heating strongly in a hard-glass test tube. The mercury is condensed on the cool portion of the tube, and the mouth of the tube contains a plug of ignited asbestos wool, which serves to keep back any particles of mercury which might be carried off; (2) estimating the chlorine in mercuric chloride by precipitation as silver chloride in the usual way, or by titration with $\frac{N}{10}$ silver nitrate. ($\frac{3}{4}$ hr. each.)

2. Does normal mercuric carbonate, $HgCO_3$, exist? Try the actions of sodium carbonate and bicarbonate on mercuric nitrate and chloride. Note that the *same* precipitate is obtained in each case, except by the bicarbonate on the chloride. Can you suggest why these substances do not react? Try mercuric cyanide, $Hg(CN)_2$, with the same reagents. Also try the action of various reagents on these three salts of mercury. It will be found that with mercuric cyanide all tests for mercury, except hydrogen sulphide, fail. Any suggestions? If not, find the specific conductivity of *equivalent* solutions of these three salts by a simple Wheatstone bridge method for electrolytes. [E. g. see *Practical Exercises in Magnetism and Electricity*, by H. E. Hadley. (Macmillan.) Experiment 102.] What do you notice? What is the explanation?

3. Try the action of potassium chromate solution on mercur*ous* nitrate. What is produced? Boil, filter and analyse the precipitate qualitatively, noting especially—

(*a*) The action of heat on the dry substance.

(*b*) Whether chromic acid is quantitatively precipitated by a mercurous salt.

Hence a useful method for estimating chromates.

4. Try the action of water on various mercurous and

mercuric salts, finally boiling with excess of water in each case. Explain.

BARIUM. Ba = 137·4.

Equivalent = 68·7. *Atom therefore divalent.*

1. *The equivalent of barium by analysis of the chloride.* Starting from *witherite* (native $BaCO_3$), prepare a *pure* specimen of barium chloride, $BaCl_2,2H_2O$.

Remember that the chief impurity is iron. Dehydrate the pure crystallised chloride by heating to about 300° C., and estimate the chlorine in a weighed portion by precipitating as silver chloride, and weighing the precipitate. Hence calculate the equivalent of barium.

2. Compare the action of potassium chromate and bichromate solutions on barium chloride solution. *N.B.*—To get a precipitate that will not pass through the filter, boil the barium solution, and add the boiling chromate solution to it dropwise, till in excess.

In each case filter and test the filtrate for barium. (How?)

Now to some more of the bichromate solution add a few cubic centimetres of concentrated sodium acetate solution, and try again. Write equations for the actions, and explain the action of the acetate.

(*N.B.*—Barium dichromate does not exist. Barium chromate only is known.) ($\frac{3}{4}$ hr.)

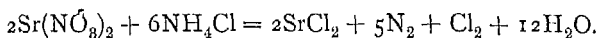
STRONTIUM. Sr = 87·6.

Equivalent = 41·9. *Atom therefore divalent.*

1. Strontianite (native $SrCO_3$) is liable to contain both ferrous and calcium carbonates as impurities. Devise a method for preparing pure strontium nitrate crystals.

Pure *anhydrous* strontium chloride can be got from this

by mixing with absolutely pure ammonium chloride (which should be resublimed) and igniting.

$$2Sr(NO_3)_2 + 6NH_4Cl = 2SrCl_2 + 5N_2 + Cl_2 + 12H_2O.$$

By estimating the chlorine in this, as silver chloride, the equivalent of strontium can be found.

N.B.—$SrCl_2,6H_2O$, the chloride obtained by the usual process, cannot be dehydrated without loss of hydrochloric acid, and some basic chloride being formed. By igniting the nitrate, or the hydrated chloride, with pure ammonium chloride, the pure anhydrous chloride is left. This is a general method for obtaining anhydrous chlorides of those *divalent* metals whose chlorides ignited alone will form basic chlorides. It fails, however, with the trivalent metals, iron (ferric), chromium, aluminium.

2. Find out the conditions under which strontium is completely precipitated from solutions of its salts by (*a*) dilute sulphuric acid; (*b*) ammonium sulphate solution, with and without the addition of dilute hydrochloric acid. Perform similar experiments with calcium, and find out under what conditions the strontium is completely precipitated, whilst the calcium is not precipitated at all, by any of these reagents. Hence separation of strontium from calcium.

CALCIUM. Ca = 40·1.

Equivalent = 20. *Atom therefore divalent.*

1. Metallic calcium is now obtainable. Devise a simple method for finding its purity, and if reasonably pure, use it for finding the equivalent. (1 hr.)

2. Hold a piece of metallic calcium in a pair of tongs, and heat it in the oxidising flame of a blast-lamp till it has burnt as completely as possible. Shake up with some *cold*

water, filter quickly, and pass carbon dioxide through the *filtrate*.

Boil the *residue* with some water. What is given off? (Smell.) Hence state what substances are produced when calcium burns in air. (20 mins.)

3. Devise a simple method of finding *approximately* the relative solubilities of (*a*) the sulphates; (*b*) the chromates; (*c*) the carbonates; (*d*) the oxalates, of barium, strontium, and calcium. What is noticeable about the results? (1 hr.)

4. *The composition of "bleaching powder."*

See Problem 12 under Estimations with $\frac{N}{10}$ thiosulphate.

GROUP III.—BORON, ALUMINIUM.

BORON. B = 11.

Equivalent = 3·67. *Atom is therefore trivalent.*

1. The equivalent may be found by turning elementary boron into the oxide B_2O_3 by heating carefully with strong nitric acid in a platinum crucible. After the boron is completely oxidised to boric acid, it is ignited strongly for some time, cooled in a dessicator, and weighed as quickly as possible.

If boron trichloride (BCl_3) is available, the equivalent can be found in a similar manner to that of phosphorus, *via* PCl_3, *q.v.* (1½ hrs.)

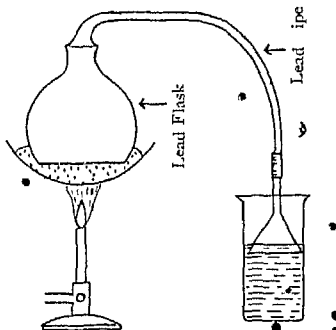



FIG. 4.

2. By heating a mixture of borax, calcium fluoride, and strong sulphuric acid in a

lead flask, investigate the action of hydrofluoric acid, etc., on boric acid. Pass the gas so obtained into water, and identify the *solid* product at any rate. Find what you can about the solution.

Neutralise with potassium carbonate, and find the action of heat on the crystallised product.

3. From borax prepare a specimen of pure crystallised boric acid. (1 hr.)

4. If boron (crude) is available, find the action of chlorine on the heated substance. If (as is most likely) boron is *not* available, a mixture of boric anhydride (B_2O_3) and carbon in the proportions $B_2O_3 : 3C$ will do just as well. This mixture is heated strongly in a combustion tube, and the product condensed in a receiver cooled by a freezing mixture. Exclude moisture rigidly from the whole apparatus, including the receiver, and beware of the vapour of the product. Find its action with water. (Care!) For apparatus, see Fig. 7.

ALUMINIUM Al = 27·1.

Equivalent = 9.03. *Atom therefore trivalent.*

1. The equivalent of aluminium is best found by determining the volume of hydrogen it displaces from fairly strong hydrochloric acid (1 : ½). The syphon-bottle method gives excellent results if all necessary corrections are made. (1 hr.)

2. From the given specimen of kaolin (aluminium silicate) prepare pure specimens of (1) alumina (Al_2O_3); (2) ammonia alum.

3. From the given specimen of bauxite (Al_2O_3) obtain a specimen of potash alum. [*N.B.*—Almost all specimens of bauxite contain ferric oxide, Fe_2O_3.]

4. Find the action of caustic soda solution, added gradu-

ally, on a solution of any aluminium salt. Compare with the corresponding action on chromium salts.

Divide the solution finally obtained into two portions. Boil one. To the other add some solid ammonium chloride and boil. Explain the action, if any. (½ hr.)

5. Find out as much as you can about the substance supplied, which is a mineral of aluminium. (1½ hrs.)

6. Find out whether normal aluminium carbonate, $Al_2(CO_3)_3$, or even a basic carbonate exists. Also try the action of a soluble sulphide on an aluminium salt. Note and explain what happens. (½ hr.)

GROUP IV.—CARBON, SILICON, TIN, LEAD.

CARBON. C = 12.

Equivalent = 3. *Atom is therefore tetravalent.*

1. Devise a method for burning pure carbon in oxygen and weighing the carbon dioxide formed. The combustion is not quite complete, and arrangements must therefore be made for the oxidation of any carbon monoxide (CO) formed. [Compare organic combustions.] The pure charcoal should be made from sugar, heating it very strongly in the absence of air till completely carbonised. The carbon so obtained should be then heated to redness in chlorine. About ·2 of a gram should be taken, weighing to 4 decimal places. Any ash left should also be weighed, and deducted from the weight of carbon. [2½ hrs., including setting up apparatus.]

2. A careful determination of the percentage of carbon dioxide in a carbonate, in one or other of the numerous pieces of apparatus designed for this purpose, should be made. (¾ hr.)

3. Saturate some strong brine with ammonia gas, and then saturate *cold* with carbon dioxide under slight pressure.

Filter and identify the precipitate, and hence explain what has happened.

4. *Examination of the carbonates of calcium.*

Compare the action of sodium carbonate and of sodium bicarbonate solutions, both cold, on some dilute calcium chloride solution (about $\frac{1}{4}$ N).

If nothing happens, boil. Is the calcium completely precipitated by either reagent? (15 mins.)

ORGANIC CHEMISTRY PROBLEMS

Below are given a few problems illustrating the methods by which the formulæ and the constitution of organic substances are arrived at. They should only be performed by students who have some fair knowledge of organic chemistry, and who have at any rate prepared a few typical organic substances, such as hydrocarbons, organic halides, esters, etc., and can identify the more common organic acids, etc.

1. *To find the formula of a hydrocarbon.*

Write down the equations for the complete combustion of several simple gaseous hydrocarbons, such as methane, ethane, ethylene and acetylene. What do you notice about the volume of carbon dioxide formed? Hence devise a general method for getting at the formula of a gaseous hydrocarbon by explosion with excess of oxygen and measuring the carbon dioxide formed and the oxygen left. [*N.B.*—An acquaintance with elementary gas analysis methods and apparatus is required for this problem.]

2. *Action of ammonia on ethyl oxalate.*

To some pure ethyl oxalate add an excess of ·880 aqueous ammonia. Filter and wash the white precipitate thoroughly, and dry it in the steam oven. Given that its molecular formula is $C_2O_2N_2H_4$, find its constitution by identifying

the products of its hydrolysis by means of caustic soda solution.

3. *Investigation of the action of alcoholic ammonia on ethyl oxalate.*

Pass dry ammonia gas into some absolute alcohol and find the increase in weight (*i. e.* the weight of NH_3 taken). Add it to some ethyl oxalate in the proportion of $NH_3 : (COOC_2H_5)_2$, *i. e.* one molecule of each.

Filter from any precipitate, and evaporate to crystallisation on a water-bath. Recrystallise from absolute alcohol, dry by pressure between filter-paper and finally in a vacuum dessicator over strong sulphuric acid, if necessary. You are required to find the constitutional formula of this substance from a knowledge of the products of hydrolysis with caustic soda solution. Its molecular formula is $C_4O_3NH_7$. Distil some with caustic soda solution and find out—

(*a*) The products of distillation.

(*b*) The residue of the flask.

4. *Constitutional formula of a substance supplied.*

You are supplied with a substance whose molecular formula is C_8H_9NO, and are required to find its constitution—

(*a*) Treat a portion in a test-tube with some strong hydrochloric acid. Warm. Cool, add caustic soda carefully till alkaline, keeping cool. What happens?

(*b*) Distil some with some fairly strong sulphuric acid (1 : 1) and identify the distillate. Also the residue if possible, by rendering alkaline with caustic soda. (CARE!)

(*c*) Distil some with concentrated caustic soda and identify the distillate.

5. *The action of fused caustic soda on a sulphonate.*

You are supplied with some sodium benzene sulphonate,

$C_6H_5SO_3Na$. Find on it the action of *gently* fused caustic soda (iron or nickel dish, and great care of hands, *eyes* and face). Pour out the fused mass on to a cold tile, and identify the products by rendering it acid with dilute hydrochloric acid.

6. *Action of dry ammonia on dry carbon dioxide.*

Pass two volumes of dry ammonia and one volume of dry carbon dioxide (as nearly as possible) into some absolute alcohol cooled with ice-water. After some time a dense mass of crystals is deposited. [Hence use wide delivery tubes.] Allow to stand for a short time, filter off by suction, and dry the crystals between filter-paper. Find out as much as you can about them by qualitative and quantitative analysis. (*N.B.*—When dissolved in water, partial, but not complete, hydrolysis takes place.)

Also try the action of an aqueous solution (cold) of the substance on some calcium chloride solution. Filter from the precipitate, and identify the precipitate. Boil the filtrate and state what occurs.

Try also the action of (*a*) nitrous acid, (*b*) hypochlorites or hypobromites on the substance. Given that its formula is $CO_2N_2H_6$, write its constitution from your experiments.

7. *Separation of benzene from a paraffin.*

Given a mixture of benzene (C_6H_6), B.P. 81° C. and light paraffin (benzolene), B.P. *about* 75–80° C., proceed to separate them. Fractional distillation is useless, on account of the nearness of their boiling points.

8. *Determination of the molecular weight of an organic acid.*

The silver salts of organic acids are all decomposed on ignition, pure silver being finally left. Give some benzoic acid, and being told that it is monobasic, find its molecular weight, by igniting a known weight of silver benzoate. Ignite carefully at first with lid on, finally to full redness,

with full access of air. A *porcelain* crucible to be used. Repeat with other organic acids, *e.g.* acetic.

9. *Distinction between primary, secondary and tertiary amines.*

You are supplied with an amine hydrochloride whose formula is $NC_3H_9 \cdot HCl$. You are required to find whether the amine is—

	Trimethylamine	$N(CH_3)_3$
	Methyl-ethylamine	$N(C_2H_5)(CH_3)H$
or	Propylamine	$N(C_3H_7)H_2$

Confirm qualitatively and quantitatively.

10. *Distinction between primary, secondary and tertiary alcohols.*

You are supplied with a butyl alcohol. *Not* knowing their boiling points, find, by a chemical method, whether it is primary, secondary or tertiary butyl alcohol.

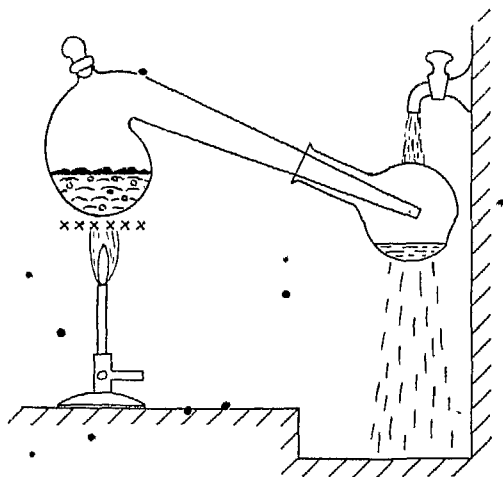



FIG. 5.

11. *Action of oxalic acid on glycerine.*

Heat some glycerine (50 grams) in a retort with an equal weight of commercial crystallised oxalic acid ($H_2C_2O_4$, $2H_2O$). The retort is connected (as shown in Fig. 5) to a receiver. What gas is evolved? Whence does it come? What will be left therefore? Allow the temperature to remain at 110° C. till the evolution of gas has slackened, and then cool to 80° C. and add another 50 grams of oxalic acid. Proceed as above, and add two more equal portions of oxalic acid in the same way. The distillate should now be identified, and one compound prepared from it. (*N.B.*—Can you recover any more of the product from the contents of the retort?)

SILICON. Si = 28·3.

Equivalent = 7·08. *Atom therefore tetravalent.*

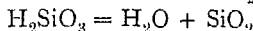
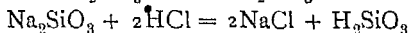
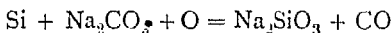
The oxide SiO_2 is acidic in properties; the hydride SiH_4 is, as usually prepared, spontaneously inflammable. Most compounds of silicon, especially silicates, are very readily acted on by hydrofluoric acid, producing silicon tetrafluoride (SiF_4), a gas.

1. *The equivalent of silicon.*

If some pure crystallised silicon is available, its equivalent can be found by oxidising it to silica (SiO_2) by the following method. Grind the silicon very finely and mix a weighed amount with about four times its weight of fusion mixture in a *platinum* crucible, and fuse gently, with free access of air, till no more carbon monoxide is evolved. The melt is cooled by dropping the crucible into a basin of cold water, and the water is then gently heated till the whole has dissolved and the crucible is removed and washed into the basin. Excess of strong hydrochloric acid is now *cautiously* added, with precautions against loss by the evolution of carbon

dioxide, and the whole evaporated dry, moistened with strong hydrochloric acid, and dried again at 120° C. The silicic acid will now be quite insoluble, and is extracted with water, filtered, washed free from chlorides, ignited strongly in a platinum crucible and weighed. Calculate the weight of silicon that combines with 8 grams of oxygen.

Equations—

$$Si + Na_2CO_3 + O = Na_2SiO_3 + CO$$
$$Na_2SiO_3 + 2HCl = 2NaCl + H_2SiO_3$$
$$H_2SiO_3 = H_2O + SiO_2$$

2. *Action of hydrofluoric acid on silica.*

Treat some sand with hydrofluoric acid, and examine the properties of the evolved gas (SiF_4), especially noting the action of water. The experiment may be done in a platinum or lead basin, and a drop of water held in the gas. Better, treat a mixture of calcium fluoride and sand with strong sulphuric acid, and pass the gas evolved into water, using a funnel as delivery tube. (See Fig 6.) Filter, and examine both the precipitate and the filtrate. Prepare the potassium salt of the acid in the filtrate, and find the action of heat on it.

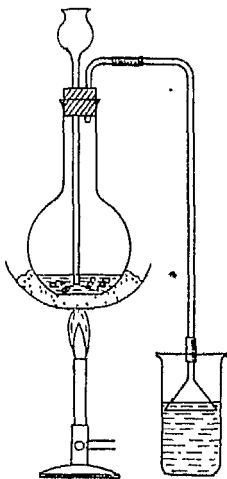



FIG. 6.

3. From results of above experiment, prepare some pure silica from kaolin. ($1\frac{1}{4}$ hrs.)

4. *Preparation of silicon from silica.*

When silica and magnesium, *both perfectly dry*, are heated together in the right proportions, silicon is obtained. *Use*

Calais sand, NOT *precipitated silica,* and carry out the heating in test-tubes about half full. The mixture should be intimate, and if no moisture is present, the action will be perfectly quiet, providing *sand* and not precipitated silica be used. If the bottom of the test-tube be heated till the action starts, it will proceed by itself. The silicon is freed from magnesium oxide and a little magnesium silicide (Mg_2Si) by extraction with dilute acid.

5. Prepare and investigate the properties of hydrogen silicide. (Care, spontaneously inflammable.)

6. Analyse qualitatively the substance supplied, noting especially the action of fused alkali on it. (1 hr.)

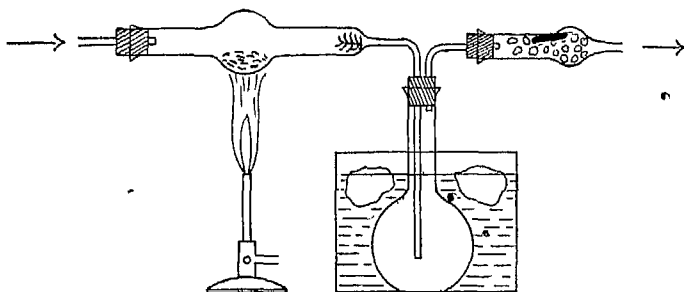



FIG. 7.

7. [To be done only under direct supervision.] Compare the actions of chlorine and of hydrochloric acid gas on heated silicon. Moisture rigidly excluded. In each case, condense the products in a receiver cooled to 0° C. Find the action of water on them (Care !), and identify the products, if possible. *Take great care not to inhale the least quantity of any of the products of these reactions.*

The experiments must be done in a good draught cupboard.

8. Find the action of a solution of any ammonium salt on a solution of a soluble silicate.

TIN. Sn = 119.

Equivalents = 59·5 *and* 29·75. *Atom therefore di- and tetravalent.*

1. The equivalent of tetravalent tin may be found by oxidising the metal with strong nitric acid, and igniting strongly the meta-stannic acid so produced. Stannic oxide (SnO_2) is left. (See "Notes on Equivalents," p. 25.)

The equivalent of divalent tin is not easy to find, as stannous oxide (SnO) is very unstable, and stannous chloride is difficult to obtain in a sufficiently pure state. The best method is to find the volume of hydrogen displaced by a known weight of tin, dissolving it in *strong* hydrochloric acid, with the aid of heat, and cooling it afterwards before taking the volume. See "Notes on Equivalents," p. 23, syphon-bottle method. (1½ hrs.)

2. Find out as much as you can about the reducing properties of stannous chloride solution. (¾ hr.)

3. Try the action of various reducing agents on stannic chloride solution. What substances reduce it? Is it a strong oxidising agent? What would you expect, from the results of Problem 2? (½ hr.)

4. *To make a "concentration" cell.*

Make a small quantity of a strong solution of stannous chloride. Place it at the bottom of a small beaker. Cautiously stratify on to it a *dilute* solution of the same substance. Now hang in the solutions a rod of tin, so that the line of separation of the two layers is about half-way up the rod. Set aside for several days. Explain, on the ionic theory, what you see.

5. The action of tin on dilute nitric acid, also a problem

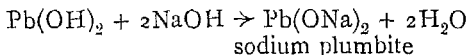
on tin-plate, will be found under Nitrogen and Iron respectively.

LEAD. Pb = 207.

Equivalents = 103·5 *and* 51·75. *Atom is di- and tetravalent.*

The oxides of lead are—

PbO, litharge, the oxide obtained by burning lead in air, and by the usual methods, *via* nitrate, carbonate or hydroxide. It is basic to acids, but is acid to caustic soda and potash, in which it dissolves.

$$Pb(OH)_2 + 2NaOH \rightarrow \underset{\text{sodium plumbite}}{Pb(ONa)_2} + 2H_2O$$

Pb_2O_3, which is got by gently oxidising sodium plumbite, $Pb(ONa)_2$, in alkaline solution, by means of hypochlorites, etc.

Pb_3O_4, red lead, or minium. Got by heating litharge to 400–450° C. in a stream of air.

PbO_2, got by the action of nitric acid on Pb_2O_3 and Pb_3O_4, or by the direct oxidation of litharge by various methods.

Pb_2O is also known. It is got by the oxalate method.

1. Find the equivalents of lead by the analysis of litharge and of lead dioxide. [See "Note on Equivalents," Part I, p. 25.] Synthesis of litharge may also be used.

2. Classify the four oxides of lead as acidic, basic or peroxides. (½ hr.)

3. Compare the action of dilute nitric acid on the four oxides of lead. Test for lead in solution in each case, and if there is any residue, identify it. Hence say what is the relation between these four oxides. Compare the oxides of manganese. (1½ hrs.)

N.B.—The lead peroxide (PbO_2) used in the above must

be *quite* pure, and free from litharge, or misleading results will be obtained.

4. *Action of chlorine water on litharge.*

Suspend litharge in hot water, and bubble in chlorine. Identify the products. Write equation. (1 hr.)

5 Prepare a specimen of lead chromate. (This is soluble in dilute mineral acids, but insoluble in acetic. Prove this.) Boil it for some time either with plenty of lime-water or with some *dilute* caustic soda. Filter. What is the filtrate? Wash the precipitate till free from alkali, and treat it as follows—

(*a*) Warm some with dilute acetic acid. What happens? Filter. Identify residue, and test the filtrate for lead.

(*b*) Warm some with dilute nitric acid. What happens? Now just neutralise with caustic soda or ammonia. What happens? Hence state clearly what is the nature of the red powder obtained by boiling lead chromate with dilute alkali. ($1\frac{3}{4}$ hrs.)

6. *Action of nitric oxide on lead dioxide.*

[*N.B.*—Do not use absolutely pure PbO_2 for this experiment; the commercial substance, which still contains some litharge, is the best.]

Set up an apparatus for passing nitric oxide over gently heated lead dioxide. [Prepare the nitric oxide by putting a mixture of ferrous sulphate and potassium nitrite in a flask, and adding strong sulphuric acid *dropwise* from a dropping funnel.] Heat the peroxide *very* gently. Identify the product of the reaction. Give equations. ($1\frac{3}{4}$ hrs.)

7. *The carbonates of lead.*

Try the actions of both sodium carbonate and bicarbonate solutions on lead nitrate solution. Does the normal carbonate, $PbCO_3$, exist, or is lead carbonate *always* basic like copper carbonate?

8. *Sensibility of tests for lead.* (½ hr.)

Devise a method for finding the limit of dilution at which hydrogen sulphide will detect lead in (*a*) acid, (*b*) alkaline solution.

9. *Properties of lead sulphate.*

Prepare lead sulphate, and find in which of the common reagents it is soluble. Also try an ammoniacal solution of ammonium tartrate.

10. Prepare some freshly precipitated lead sulphide in the usual way.

(*a*) Treat a portion of it in a porcelain basin with hot nitric acid (2 acid : 1 water). Filter, and wash residue with hot water till filtrate is free from lead. See if any lead sulphate is left in the residue (see Problem 9). Explain its presence.

(*b*) Treat a second portion with more dilute hot nitric acid (1 acid : 2 water), and examine as in (*a*). Explain.

(*b*) Suspend a third portion in hot water, and *very gradually* add hot, strong nitric acid. Examine residue as before. Explain. Hence explain the best way to separate lead sulphide from mercury sulphide in Group II. (1 hr.)

GROUP V.—NITROGEN, PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH.

NITROGEN. N = 14.

Equivalents = 4·67 *and* 2·8. *Atom therefore tri- and pentavalent.*

1. The equivalents of nitrogen may be found—

(*a*) By a determination of the percentage composition of ammonia by weight. This gives the equivalent of trivalent nitrogen.

(*b*) By a determination of the percentage composition

by weight of ammonium chloride, giving the equivalent of pentavalent nitrogen.

(*a*) should be done by a gravimetric method. [Try the action of dry ammonia on heated copper oxide.]

(*b*) is most easily done by a volumetric method.

2. *Action of zinc dust and alkali on a nitrate.*

Find the action of zinc dust or filings on a solution of sodium or potassium nitrate, made alkaline with caustic soda. [Remember $Zn + 2NaOH = Zn(ONa)_2 + 2H$.] Find to what the nitrate is reduced.

3. Find the action of zinc on *dilute* nitric acid. Investigate the gaseous products and the residual solution.

4. Find the action of nitric oxide (NO) on nitric acid of various strengths. Bubble the gas through the acid, with precautions to keep out air. (1½ hrs.)

5. Pass nitrogen peroxide (from *dry* heated lead nitrate) into dilute potash. Find what substances are formed. (1 hr.)

6. See under Arsenic, Problem 2.

7. You are given two crystalline salts. Find as much as you can about them, whether they are reducing or oxidising agents, powerful or weak, and anything else that may occur to you. What are the two substances? (1½ hrs.)

8. *Reduction of nitric acid by nascent hydrogen.*

Treat some metallic tin with dilute hydrochloric acid (1 : 1), and as soon as action sets in, add about half as much dilute nitric acid of an equivalent strength (1 : 3 will be about right). When all the tin has dissolved (*gentle* heat may be applied) remove it from solution by precipitating as the sulphide by a stream of hydrogen sulphide. Filter, evaporate the filtrate dry on a *water*-bath, and extract with absolute alcohol. Evaporate the alcohol, and find out as much as you can about the substance left. Also find out what you can about the substance *insoluble* in alcohol.

What do you think they are? Remember they will most probably be reduction products of the nitric acid.

N.B.—It is no use performing the above preparation on too small a scale. Use about 30 grams of tin and a corresponding amount of the other substances. ($2\frac{1}{2}$ hrs.)

9. *Oxidation of ammonia in the presence of platinum.*

When a red-hot platinum wire is introduced into a mixture of ammonia and air, it continues to glow. Devise an apparatus by which a stream of the mixture of ammonia and air may be supplied to the glowing wire, and the products of oxidation led into some dilute potash or soda. Find out to what state the ammonia is oxidised. (1 hr.)

Platinised asbestos acts similarly, but better. Devise a method for comparing the efficiencies of the two forms of catalyst.

10. *Action of hydroxylamine on iron compounds.*

To a little freshly-made ferrous sulphate solution add some caustic soda solution to precipitate ferrous hydroxide. Add now a solution of a salt of hydroxylamine, and warm. Note what happens. Boil and smell the steam. Has the hydroxylamine been reduced? Now acidify and add some more of the hydroxylamine solution. What becomes of the iron? Give equations. (15 mins.)

PHOSPHORUS. P = 31.

Equivalents = 10·3 and 6·2. Atom therefore tri- and pentavalent.

1 Devise a method for finding the equivalent of trivalent phosphorus. Try the action of phosphorous chloride, PCl_3, on water. ($1\frac{1}{2}$ hrs.)

2. *The phosphoric acids.*

Obtain some orthophosphoric acid solution (H_3PO_4). Evaporate some carefully and heat the residue to 255° C.

for some time. Meanwhile neutralise a portion of the ortho-acid with ammonia or sodium carbonate, and test the solution with (*a*) silver nitrate solution; (*b*) barium chloride solution Also test the free acid with a *dilute* solution of egg albumen.

Take a portion of the residue that has been heated to 255° C., and dissolve in *cold* water, neutralise with ammonia (avoid excess, as it may not be heated), and try the above tests on the neutral solution

Heat the remainder of the residue to dull redness for some time, dissolve in a little cold water, neutralise, and apply the above tests. The products of heat on orthophosphoric acid are respectively pyrophosphoric acid, $H_4P_2O_7$, and metaphosphoric acid, HPO_3. Draw up a scheme for distinguishing between the three acids from your results.

3. *Action of heat on some phosphates.*

Find the action of heat on the following phosphates: sodium hydrogen phosphate ($Na_2HPO_4,12H_2O$); sodium dihydrogen phosphate (NaH_2PO_4); magnesium ammonium phosphate ($MgNH_4PO_4,6H_2O$). Identify both the volatile and non-volatile products in each case, and confirm by a roughly quantitative experiment. Write the equations. See also Problem 3 under Magnesium. (2 hrs.)

4. *Preparation of microcosmic salt, and the action of heat on it.*

Given some orthophosphoric acid, devise a method for preparing microcosmic salt ($NaNH_4HPO_4,4H_2O$). (See Introduction on preparation of salts, p. 8.) Obtain crystals, and find the action of heat upon them, identifying both volatile and non-volatile products. Hence write an equation for the action of heat, and confirm by a roughly quantitative method. (2 hrs.)

5. *Phosphoric acid and phosphates from bone-ash.*

Given some bone-ash [$Ca_3(PO_4)_2$ + some $CaCO_3$], prepare specimens of ammonium dihydrogen phosphate ($NH_4H_2PO_4$) and ammonium hydrogen phosphate [$(NH_4)_2HPO_4$]. Find the action of heat on them, and identify all products. Give equations. (2 hrs.)

6. *Action of phosphorus on alkalis.*

A solution of barium hydroxide (1 in 10) is boiled with yellow phosphorus, using 1 gram of phosphorus to every 4 grams of barium hydroxide. (About 1½ litres of the liquid should be taken.) A large round-bottomed flask of *at least* 2 litres capacity is used, and the boiling is continued on a

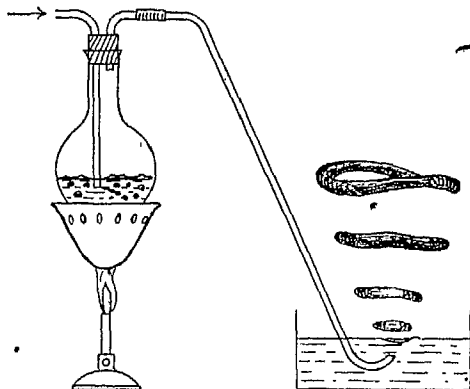



FIG. 8.

sand-bath or a Babo's safety air-bath till all the phosphorus has gone into solution. As phosphine (PH_3), which is spontaneously inflammable, is evolved, the air in the flask must be replaced by coal-gas, and the whole operation conducted in a draught cupboard. A delivery-tube leads the phosphine into a basin of water, where each bubble inflames harmlessly as it bursts.

When all the phosphorus has dissolved, filter the solution, heat it in a large basin, and pass in carbon dioxide till all the excess of baryta is precipitated as barium carbonate. Filter, and wash the residue with small quantities of boiling water, which are added to the filtrate.

Now evaporate the whole filtrate considerably, filter again if more barium carbonate comes down, and continue the evaporation till crystallisation begins. Now add some alcohol, drain the crystals on the pump, and obtain a further crop of crystals from the mother liquor. Recrystallise the whole product from water.

About 50 grams of a beautifully crystalline salt will be obtained. Find the action of heat on the dried crystals, identifying both the residue and volatile products. What is it? Find also as much as you can about the properties of the substance; *e. g.* is it an oxidising or reducing agent, and what are the products of oxidation or reduction, as the case may be? Also try the action of the solution on silver nitrate and on mercuric chloride solutions, also on hot strong potash solution.

7. *Reduction of copper salts by hypophosphorous acid.*

From some 5 per cent. barium hypophosphite solution obtain the free acid by adding exactly the right amount of 4N sulphuric acid and filtering from the precipitated barium sulphate. Add to the clear filtrate some 25 per cent. copper sulphate solution, and allow to stand for some time at the room temperature. If nothing happens, heat to 30° C., and filter and wash the precipitate. Dry it *in vacuo*. Try on it—

(*a*) The action of heat. What is evolved and what left?

(*b*) The action of a little strong hydrochloric acid.

Identify the products, if possible, and say what the substance is. ($\frac{3}{4}$ hr.)

8. *Reducing powers of phosphorous and hypophosphorous acids.*

Compare the reducing actions of phosphorous and hypophosphorous acid solutions.

Try with each—

(*a*) Strong sulphuric, and warm.
(*b*) Silver nitrate solution.
(*c*) Copper sulphate solution.
(*d*) Mercuric chloride solution.
(*e*) Strong potash, and warm.
(*f*) Ignition of the solid acid.
(*g*) Sulphurous acid.

N.B.—If no phosphorous acid is at hand, it can be readily prepared by adding phosphorous chloride to water, evaporating dry, and cautiously heating to 180° C. ($\frac{3}{4}$ hr.)

ARSENIC. As. = 75.

Equivalents = 25 *and* 15. *Atom therefore tri- and pentavalent.*

The oxides are As_2O_3 and As_2O_5, both acid anhydrides, and very like the corresponding oxides of phosphorus.

N.B.—*In working the following problems, remember that all volatile compounds of arsenic are exceedingly poisonous, and great care must be taken not to inhale the least quantity of any of them.*

1. Devise a method for finding the equivalent of trivalent arsenic. (See equivalent of phosphorus.) For equivalent of pentavalent arsenic, see Problem 2, and also Problem 1 under Antimony.

2. Find the action of fairly strong nitric acid (1 : 1) on arsenious oxide (As_2O_3). Pass the evolved gas through a U-tube immersed in a freezing mixture, and identify it by dissolving the liquefied gas in dilute ice-cold sodium

carbonate solution. Also identify the *dried* residue, by exactly neutralising some with sodium carbonate solution and adding silver nitrate. Apply other tests in confirmation. Write an equation representing the action. *N.B.*—When drying the residue, drive off the excess of nitric acid on a sand-bath, but do not heat to a higher temperature than necessary for this purpose What is the action of strong heat on this residue? (2 hrs.)

3. See Problem 4 under Magnesium.

4. Find the action of arsenic hydride (AsH_3) (from zinc, dilute sulphuric acid, and a little arsenious acid) upon silver nitrate solution. Wash the precipitate thoroughly and identify it by qualitative analysis. Also identify the contents of the filtrate, and find out what has become of the arsenic. (1 hr.)

(*N.B.*—Arsine is a powerful poison.)

ANTIMONY. Sb = 120

Equivalents = 40 *and* 24. *The atom is therefore tri- and pentavalent.*

The oxides of antimony are—

Sb_2O_3, antimonious anhydride, acidic mostly, but basic to strong acids.

Sb_2O_5, antimonic anhydride, acidic.

Sb_2O_4, antimony tetroxide, neutral.

1. *The equivalents of antimony.*

(*a*) Find the equivalent of trivalent antimony by a gravimetric determination of the chlorine in antimonious chloride, $SbCl_3$, by solution in water, and addition of plenty of dilute nitric acid (to prevent silver antimonite being precipitated) and silver nitrate.

(*b*) Find the equivalent of pentavalent antimony by synthesis of the pentoxide Sb_2O_5 by the direct action of

strong nitric acid on antimony (see p. 25). The antimony is converted into metantimonic acid, $HSbO_3$, which on being heated to a temperature *not exceeding* 270 °C is dehydrated thus: $2HSbO_3 = H_2O + Sb_2O_5$.

2. *Action of stibine (SbH_3) on silver nitrate solution.*

Find the action of stibine (from pure zinc, dilute sulphuric acid, and a little antimony solution of any kind) on silver nitrate solution. Identify both the precipitate and the filtrate by careful qualitative analysis, and find out what has become of the antimony. Do any quantitative confirmatory tests that you can perform simply and easily. Compare with the action of arsine on silver nitrate. (2 hrs.)

(*N.B.*—Stibine is very poisonous.)

BISMUTH. Bi = 208.

Equivalents = 69·3 *and* 41·6. *Atom is therefore tri- and pentavalent.*

The oxides are Bi_2O_3 and Bi_2O_5. The former is purely basic, the latter probably acidic. See below.

1. Find the equivalent of bismuth by the oxide method, *via* the nitrate. See "Notes on Equivalents," p. 25, for details. (1 hr.)

2. *Properties of bismuth iodide.*

To a solution of bismuth nitrate add potassium iodide solution gradually till in excess. Note everything that happens.

Now pour the solution into a gas jar, and *gradually* add cold water, till the water is in *large* excess. Note each stage of the happenings. Try and explain. (15 mins.)

3. *Oxidation of bismuth by the halogens in alkaline solution.*

To some very strong potash or soda solution add some bismuth nitrate solution, and saturate the liquid, which contains bismuth hydroxide, $Bi(OH)_3$ [or $BiO(OH)$], with

either chlorine, bromine, or hydrogen peroxide. The precipitate should turn brown.

Filter and wash the precipitate thoroughly, and dry it in the steam oven, finally at 120° C. Find the action of heat on it, identifying both volatile product and residue. What do you think the brown substance is?

4. See if normal bismuth carbonate $Bi_2(CO_3)_3$ exists, or whether bismuth forms only basic carbonate, or no carbonate at all. What would you expect, from the ready hydrolysis of other bismuth salts?

(Bi_2O_3 is a very feeble base.)

5. *Reduction of bismuth compounds by alkaline stannite.*

To a solution of sodium stannite (cold)—got by adding caustic soda to stannous chloride solution till the precipitate formed at first redissolves—add a solution of a bismuth salt. Identify the precipitate, and state what you would expect to have happened to the tin. Try and confirm.

6. *A test for potassium.*

To some bismuth chloride solution (a fair amount) add plenty of sodium thiosulphate solution and some alcohol. If a precipitate forms, clear by the cautious addition of water and filter if necessary. Now add it to a strong solution of potassium chloride. Filter, wash the yellow precipitate with alcohol, and identify it.

Hence note a useful test for potassium (in the absence of ammonium salts).

GROUP VI.—OXYGEN, SULPHUR, CHROMIUM

OXYGEN. O = 16.

Equivalent = 8. Atom is therefore divalent.

1. The equivalent of oxygen may be found in a variety of ways—either by the synthesis of water, by passing hydrogen

over red-hot copper oxide, and weighing the water formed and the oxygen in it (*i. e.* the loss of the copper oxide), or by analysis or synthesis of a metallic oxide, the equivalent of the metal being assumed.

The latter method is the most suitable from a student's point of view, but the former should be carried out, using a simplified apparatus on the lines of Dumas'.

(See any Inorganic Chemistry.)

2. *Classes of peroxides.*

Compare the action of hot strong hydrochloric acid on the following peroxides: MnO_2, PbO_2, BaO_2 and Na_2O_2. (*Care with the last!*) What comes off? Also try cold dilute HCl, filter, and test the filtrates for an oxidising agent. How do they differ? Remembering that manganese and lead are both capable of exerting higher valency, $MnCl_4$ and $PbCl_4$ being probably formed, what do you think is the graphic formula of each of the above peroxides?

3. Numerous examples of oxidation actions will be found under Chlorine, Bromine, Iodine, Lead, Chromium, Iron, Manganese, $\frac{N}{10}$ Permanganate, $\frac{N}{10}$ Dichromate, and $\frac{N}{10}$ Thiosulphate.

4. Find the action of hydrogen peroxide solution on the following substances—

(*a*) Potassium permanganate and dilute sulphuric acid.

(*b*) Freshly precipitated silver oxide (got thus: $2AgNO_3 + 2NaOH = Ag_2O + 2NaNO_3 + H_2O$).

(*c*) Potassium dichromate solution (a few drops) acidified with dilute sulphuric acid. Shake up the resulting liquid with ether.

(*d*) Potassium iodide solution.

(*e*) Platinum black.

(*f*) Silver leaf.

(*g*) Mercury.

(*h*) Lead sulphide, precipitated on a filter-paper and dried.

(*i*) Potassium ferrocyanide.

Classify the reactions of hydrogen peroxide. (1½ hrs.)

5. Set up an apparatus for feeding the *luminous* flame of a bunsen burner with oxygen. The oxygen to be introduced into the air-hole at the base of the burner, and the rate to be capable of nice regulation. Describe and explain everything that happens, starting with a very slow stream of oxygen, and gradually increasing it. (1½ hrs.)

6. *Oxidising power of electrolytic oxygen.*

In an electrolytic cell for the electrolysis of dilute sulphuric acid, construct the anode of the following substances—

(*a*) Gas-carbon, (*b*) copper, (*c*) iron, (*d*) manganese (or ferromanganese will do), (*e*) lead.

Note what happens in each case when the current is passed. Does the oxygen act on the anode, and if so, to what state is it oxidised?

N.B.—In the case of (*c*) and (*d*), electrolyse caustic soda solution instead of dilute sulphuric acid.

SULPHUR. S = 32·1.

Equivalents = 16·05, 8·02 and 5·35. *Atom therefore di-, tetra-, and hexavalent.*

1. The equivalent of tetravalent sulphur may be found by burning sulphur in a stream of oxygen and absorbing the dioxide formed in a U-tube of soda-lime. The divalent equivalent may be found by direct synthesis of cuprous sulphide, Cu_2S. (See under Copper.)

2. For problems on the oxidation of sulphur dioxide by various reagents, see under Chlorine, Bromine, Iodine, etc.

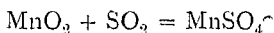
Reduction of sulphurous acid.

3. Find the action of a strong solution of sulphur dioxide in absolute alcohol on metallic zinc. Arrange to keep out of contact with air. Find out as much as you can about the properties of the product. Test with various oxidising and reducing agents, etc. Compare the action of sulphurous acid on magnesium.

3a. Electrolyse a saturated solution of sodium hydrogen sulphite, and examine any precipitate that forms at the cathode. (Reduction product of sulphurous acid by nascent hydrogen.) If no precipitate, examine the cathode liquid. Arrangements should be made to keep the cathode liquid separate from the rest of the cell.

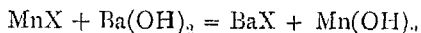
4. *To examine the action of sulphur dioxide on manganese dioxide.*

If sulphur dioxide is passed through a suspension of manganese dioxide in water, part is absorbed according to the following—

$$MnO_2 + SO_2 = MnSO_4.$$

If, however, the temperature is kept low, very little manganous sulphate is obtained, and another reaction takes place. Investigate this by the following method.

Either prepare some freshly precipitated manganese dioxide [$MnO(OH)_2$], or *better*, grind up some manganese dioxide very finely, and levigate it. Use the finest portions only. Take a fair amount of the slime so obtained, suspend it in water, surround it with ice, and pass in sulphur dioxide from a syphon of the liquefied gas. When all the manganese dioxide has dissolved, add baryta-water till the solution is alkaline, warming very gently at the same time. This precipitates any manganous sulphate that has formed [as $Mn(OH)_2$ and $BaSO_4$], thus getting rid of it. At the same time the

other manganese salt that has been formed is transformed into its barium salt, which is soluble and more easily crystallised than the manganous salt.

$$MnX + Ba(OH)_2 = BaX + Mn(OH)_2$$

Get rid of excess of baryta by passing carbon dioxide through the hot liquid. Filter and crystallise out the barium salt. You are required—

(*a*) To investigate the action of heat on this salt, identifying both the residue and the volatile products.

(*b*) To investigate the action of dilute acids on it, first cold, then hot, with a view to seeing what the free acid is like.

Say what you think the substance is; and if you can suggest any quantitative confirmation, carry it out.

N.B.—*The above preparation requires some time, and during the long intervals of waiting some other experiment should be proceeded with.*

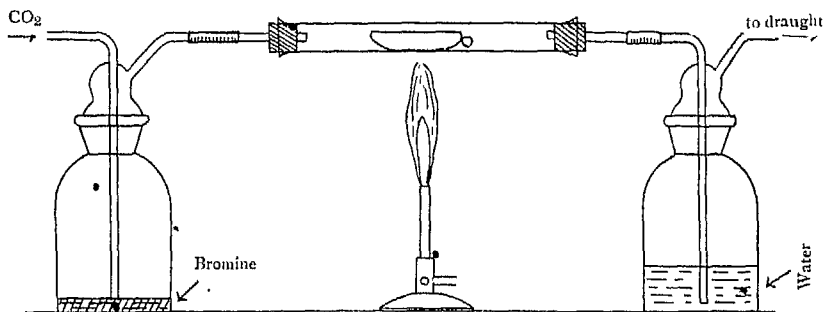



FIG. 9.

5. *Action of bromine on metallic sulphides.*

Arrange an experiment to pass bromine over some powdered galena (PbS). The galena is contained in a porcelain boat, in a combustion tube, and is gently heated whilst the

bromine, carried over by a stream of carbon dioxide, passes over it. Pass the products of the action in water. Examine this water, any liquid produced in the tube, and the residue in the boat. ($1\frac{1}{2}$ hrs.) (See Fig. 9.)

Compare with the action of bromine on stannic sulphide (SnS_2). Artificial "mosaic gold" may be used. What do you think becomes of—

(*a*) The tin; (*b*) the bromine; (*c*) the sulphur?

6. Find the action of heat on powdered sodium sulphite crystals. Do the experiment in a covered crucible, heating gently at first till the water of crystallisation has come off, then very strongly for some time. Identify the products of the action. ($1\frac{1}{4}$ hrs.)

7. Find the action of heat on powdered sodium thiosulphate crystals similarly to Problem 6. ($1\frac{1}{4}$ hrs.)

To what class of reaction do these two belong? Quote other examples you have come across.

8. *Electrolysis of potassium bisulphate.*

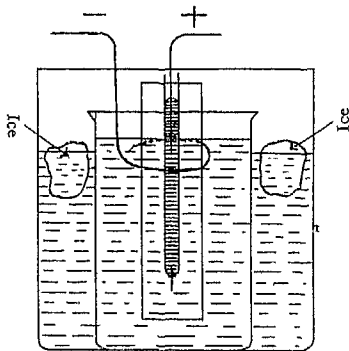



FIG. 10.

Arrange an experiment to electrolyse a saturated solution of potassium bisulphate ($KHSO_4$), with a very small anode, the anode liquid to be separated from the rest, and the whole to be kept cool. The apparatus shown may be used, and a current of 1 amp. should be employed. The anode is about 2 mm. of platinum wire projecting from a tube filled with mercury, which serves to make connection.

The cathode is a ring of platinum or copper wire near

the surface of the liquid, to avoid disturbance of the solution by the bubbles of hydrogen. After some time, crystals will be deposited from the cathode liquid. When a fair yield is obtained, filter off rapidly by suction, dry on a porous plate, and find out as much as you can about the properties of the crystals.

CHROMIUM. Cr = 52.

Equivalents = 17·3 *and* 8·65. *Atom therefore tri- and hexavalent.*

The oxides of chromium are chromic oxide, Cr_2O_3, basic; chromic anhydride, CrO_3, acidic.

Cr_2O_3 gives rise to the ordinary chromic salts. It is, however, practically insoluble in any acid if it has been recently ignited. In the form of its hydrate, $Cr(OH)_3$, it is readily soluble in acids.

CrO_3 gives rise to the chromates and dichromates, which are analogous to the sulphates and pyrosulphates.

Chromous salts, corresponding to an exceedingly unstable oxide CrO, are known, but are immediately oxidised to the chromic state by atmospheric oxygen.

The question of the conditions affecting the oxidation of Cr_2O_3 to CrO_3 and the reduction of CrO_3 to Cr_2O_3 is of great interest and importance.

1. The equivalent of trivalent chromium may be found by synthesis of the oxide Cr_2O_3, *via* the nitrate.

2. Given a chromic salt, prepare a specimen of the oxide Cr_2O_3.

3. Given some potassium dichromate, prepare a specimen of chromic anhydride, CrO_3.

N.B.—Try, in a wide test-tube, the action of strong sulphuric acid on the concentrated dichromate solution.

To prepare the oxide in quantity, add *carefully* between double and treble the theoretical amount of sulphuric acid to a strong solution of the bichromate. Leave overnight for the potassium bisulphate ($KHSO_4$) to crystallise out. Decant off the solution and evaporate on the *water-bath* to crystallisation of the chromic anhydride. How can you purify it?

4. *Oxidation of chromic hydrate in alkaline solution.*

To a solution of a chromic salt add, drop by drop, some caustic soda, cold, till the latter is in excess. Note exactly what happens. Divide the solution into several portions and treat them as follows—

(*a*) Boil. Explain the action. Allow to cool, and explain.

(Compare a similar experiment with aluminium. Hence draw up a scheme for the separation of chromium and aluminium.)

(*b*), (*c*), (*d*), etc. Treat with various oxidising agents, as chlorine, bromine, hypochlorites, hydrogen peroxide, lead peroxide, etc. What does the resulting solution contain? Give equations. (1 hr.)

5. *Oxidation of a chromic salt in neutral solution.*

To a solution of a chromic salt (*e.g.* $CrCl_3$), add some *freshly precipitated* manganese dioxide [$MnO(OH)_2$] which has been obtained by adding caustic soda to a manganous salt, and oxidising the precipitated manganese hydrate by bromine water or hydrogen peroxide, filtering and washing thoroughly.

Warm the mixture; finally raise to a boil, the manganese dioxide being kept in excess.

Filter. Test the filtrate with litmus. How does its reaction compare with that of the original chromium solution? Note the *colour* of the filtrate. What does it contain?

Try and give an equation, and confirm your deductions by testing the filtrate for the substances you think may have been formed.

[*N.B.*—This experiment may be left till the study of the oxides of manganese has commenced. See Problem 7 under Manganese.]

6. What substances are formed when—

(*a*) Potassium chromate solution is acidified with any acid?

(*b*) Potassium dichromate solution is rendered alkaline?

From your results, given a mixture of potassium chromate and dichromate, devise a simple method of finding approximately the weights of each in the mixture.

7. *Reduction of chromates to chromic salts.*

Remembering that as shown in 4 (*b*), (*c*), (*d*), etc., chromic oxide is readily oxidised to chromic acid in *alkaline* solution, compare the reducibility of chromic acid in *acid* solution, thus—

To a solution of potassium dichromate add dilute sulphuric acid, and—

(*a*) A ferrous salt; (*b*) hydrogen sulphide; (*c*) sulphur dioxide; (*d*) potassium iodide; (*e*) potassium bromide, and warm; (*f*) strong hydrochloric acid, and heat; (*g*) alcohol, and warm; (*h*) oxalic acid, and boil. Identify products in each case and give equations. (1 hr.)

8. *Oxidation of chromic salts in* ACID *solution.*

(*a*) To a solution of chromic chloride (or sulphate) add chlorine and heat. Is there any action? (Cf. Problem 4.) Why do you think nothing happens? [See 7 (*f*).]

(*b*) To a solution of chromic chloride (or sulphate) add an excess of a strong sodium acetate solution, warm, and pass in chlorine. What happens? Avoiding excess of chlorine, compare the reaction to litmus of the original

solution and the final solution. With what is it acid? To what state has the chromium been oxidised? Hence derive an equation. (First work it out by simply considering the initial and final states of oxidation of the chromium, and then add the part played by the sodium acetate.) (1 hr.)

9. Find what happens when the following chromates are ignited—

(*a*) Ammonium chromate; (*b*) ammonium dichromate (care: use a little only); (*c*) potassium chromate; (*d*) potassium dichromate; (*e*) mercurous chromate (prepared by adding potassium chromate to a solution of a mercurous salt).

10. *On the precipitation of the CrO_4 ion by lead.*

Take or prepare a little lead chromate, and find in what reagents it is soluble. (Try dilute mineral acids, dilute acetic acid, etc.)

Now to a solution of lead *acetate* add some potassium dichromate solution, keeping the lead salt in slight excess. Is the precipitation of the CrO_4 ion complete? Test the clear filtrate for CrO_4 and for a free acid. Write an equation.

Now repeat *exactly*, using lead *nitrate* instead of acetate, being careful to keep the lead salt in slight excess. Is the CrO_4 completely precipitated? Does the filtrate contain a free acid? Write an equation to explain your observations. To some more lead nitrate solution add some fairly strong sodium acetate, and again see if you can completely precipitate the CrO_4 ion.

Explain clearly the function of the sodium acetate.

Compare the action of barium chloride on potassium chromate and dichromate, with and without sodium acetate. (See under Barium.) (1 hr.)

GROUP VII.—FLUORINE, CHLORINE, BROMINE, IODINE, MANGANESE

FLUORINE. F = 19.

Equivalent = 19. *Atom therefore monovalent.*

1. The equivalent of fluorine cannot be easily found by the student, unless some pure fluoride is available which is soluble in water. Silver fluoride, AgF, is *soluble*, and by a determination of the percentage of silver in it, by precipitation as silver chloride, the equivalent of fluorine may be calculated. Analysis of pure potassium fluoride, KF, if available, may be used. By cautious ignition, in a platinum crucible, with strong sulphuric acid, the potassium may be converted into potassium sulphate, K_2SO_4, in which form it can be weighed and the percentage of potassium in the fluoride deduced. Hence the equivalent. Another method that may be employed is the determination of the calcium in pure fluorspar, CaF_2, for which see a good book on Quantitative Analysis.

2. For several problems involving fluorine or its compounds see under Boron and Silicon.

CHLORINE. Cl = 35·5.

Equivalent = 35·5. *Atom therefore monovalent.*

1. The equivalent may be found either by the analysis or synthesis of any chloride, and the weight of chlorine combined with one equivalent of the metal can be calculated. Try (*a*) the volumetric analysis of pure sodium chloride; (*b*) the synthesis of silver chloride by passing pure dry chlorine over "molecular" silver (*i. e.* silver precipitated by a reducing agent from silver nitrate). In the latter case heat is unnecessary.

2. Pass chlorine into some sulphurous acid and find out what happens. Give an equation. ($\frac{1}{2}$ hr.)

N.B.—*A steady stream of chlorine can be easily prepared by dropping strong hydrochloric acid from a dropping-funnel on to solid potassium permanganate. Towards the end heat on a sand-bath.*

3. Pass chlorine into some fairly strong potassium bromide solution till the action appears to be *just* over. Keep it cool with ice all the time. To a small quantity of the product add *gradually* sulphurous acid solution. Explain everything you observe. Neutralise most of the main portion with *potash*, and evaporate carefully to crystallisation. What crystallises out, and what is left in solution? Find also the general properties of the remaining portion of the solution. (2 hrs.)

4. Repeat (3) exactly with potassium *iodide*. (2 hrs.)

5. Pass chlorine over some *very gently* heated silver bromide contained in a porcelain boat in a tube. (Temperature not to exceed 100° C.) Avoid excess of chlorine escaping into the room. Describe all you observe, and give equations and confirm quantitatively. Heat the residue in the boat in a stream of hydrogen, and find out what happens. Is this method available for finding the equivalent of chlorine?

6. See Problem 12 under $\frac{N}{10}$ Sodium thiosulphate.

7. *Action of chlorine on a thiosulphate.*

Pass chlorine into a solution of sodium thiosulphate till the solution *just* smells permanently of chlorine. Remove the smell by adding dropwise some more dilute thiosulphate. Find out the products of the reaction, and compare with the action of bromine on thiosulphate (Problem 8 under Bromine) and iodine on thiosulphate (see under Estimations with $\frac{N}{10}$ Sodium thiosulphate). (1 hr.)

8. Compare quantitatively the oxidising power of a known volume of chlorine water with that of the solution obtained by adding the same volume of chlorine water to an equivalent amount of cold potash solution (Cl_2 : 2KOH). ($1\frac{3}{4}$ hrs.)

BROMINE. Br = 80.

Equivalent = 80. *Atom therefore monovalent.*

1. *To find the equivalent of bromine.*

The equivalent of bromine may be found by determining the percentage of bromine in pure potassium bromide, by means of a $\frac{N}{10}$ solution of silver nitrate, and calculating the weight of bromine that combines with the equivalent weight (39 grams) of potassium. (1 hr.)

2. *Some oxidising actions of bromine.*

Pass bromine vapour (best by bubbling carbon dioxide through some bromine contained in a gas wash-bottle) into solutions of (*a*) hydrogen sulphide, (*b*) sulphur dioxide. Explain the action in each case, having identified the products of the reaction. (1 hr.)

3. *Action of bromine on an iodide.*

To a small quantity of a dilute solution of potassium iodide in a boiling tube add some chloroform or carbon disulphide. Now add bromine water gradually, shaking well between each addition, and explain exactly what happens.

4. *Action of bromine on silver iodide.*

Pass bromine vapour (by means of a stream of carbon dioxide) over some very gently warmed (100° C.) silver iodide, contained in a porcelain boat in a tube. Describe and explain everything that happens, and confirm quantitatively.

5. From the results of Problems 5 under Chlorine and 4 under Bromine, devise a method for finding the percentage

weight of each substance in the mixture of silver chloride, bromide and iodide with which you are supplied.

6. Devise and carry out a method for the preparation of potassium bromate and potassium bromide from caustic potash and bromine.

7. See Problems 2, 11 and 13 under $\frac{N}{10}$ Sodium thiosulphate, pp. 103–5.

8. *Action of bromine on a thiosulphate.*

To a solution of sodium thiosulphate add bromine, cautiously, till the last drop gives a permanent yellow tinge, and *just* destroy this tinge again by adding dilute thiosulphate dropwise. Test the liquid with litmus, and identify as far as possible its contents. Also distil about three-quarters of it, and find out whether anything besides water passes over. Test the distillate with litmus paper, and then identify the contents. Write the equation for the action of bromine on sodium thiosulphate. Compare with the action of iodine on sodium thiosulphate as given under $\frac{N}{10}$ Thiosulphate titrations, p. 103. (1 hr.)

IODINE. I = 127.

Equivalent = 127. *Atom therefore monovalent.*

1. Determine the equivalent of iodine by finding the percentage composition of pure potassium iodide by means of a $\frac{N}{10}$ silver nitrate solution (see p. 100). Hence calculate the weight of iodine that combines with 39·1 grams of potassium.

2. *Some oxidising actions of iodine.*

Find the action of iodine (finely powdered and suspended in water) on—

(*a*) Hydrogen sulphide. (*b*) Sulphur dioxide.
(*c*) Chlorine.

In each case bubble the gas into the suspension until the iodine has *almost* disappeared, and filter from excess of iodine. Identify the products and write equations.

In (*c*) it may be of assistance, in identifying the products, to test a portion of the liquid with sulphurous acid. (1 hr.)

3. *Action of iodine on a chlorate.*

N.B.—*Perform this experiment in a good draught cupboard.*

Weigh out portions of potassium chlorate and iodine in the proportions $2KClO_3 : I_2$, taking about 10 per cent. more iodine than demanded by the above ratio, to compensate for loss by volatilisation.

Dissolve the chlorate in not too much hot water, and to the warm liquid, contained in a large beaker, add the powdered iodine. (Excess is used to compensate for a little loss by volatilisation.) Add now a few drops of strong nitric acid. [*N.B.*—This is merely to help the action to start.] Describe exactly what happens. When the somewhat violent action is over, boil the liquid, and allow to crystallise. Identify the substance that crystallises out [after at least *one* recrystallisation].

4. *Oxidation of iodine by nitric acid.*

Find the action of the strongest fuming nitric acid on powdered iodine. [Use 15 grams of iodine and 100 c.c. of the acid.] Use a flask and a sand-bath in the draught cupboard, and add the iodine *slowly*. When it has all dissolved, dilute the liquor with its own volume of water, evaporate on a sand-bath to a quarter of its volume, and set aside to crystallise. Identify the crystals, and find the action on them of (*a*) heat, (*b*) potassium iodide solution, (*c*) sulphurous acid solution.

5. See also Problem 5 under Manganese and numerous problems under $\frac{N}{10}$ Sodium thiosulphate titrations, dealing with the oxidations and reductions of iodine, etc.

MANGANESE. Mn = 55.

Equivalents = 27·5 *and* 13·75. *Atom therefore di- and tetravalent.*

The oxides of manganese are exceedingly interesting and of theoretical and practical importance.

The known oxides are—

MnO, manganous oxide.
Mn_2O_3, manganic oxide.
Mn_3O_4, mangano-manganic oxide.
MnO_2, manganese dioxide, or manganous anhydride.
Mn_2O_7, permanganic anhydride.

MnO_3 has not been prepared, but salts corresponding to it are known, *e.g.* K_2MnO_4, potassium manganate.

The salts of manganese nearly all correspond to the oxide MnO, which is entirely basic. The manganic salts, from Mn_2O_3, are very unstable (cf. ferrous and ferric salts), but manganese ammonium alum, $Mn_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$, is fairly stable.

MnO_2 is purely acid, giving rise to the manganites of which "Weldon Mud" (calcium manganite) is the best known. MnO_3 gives rise to manganates and Mn_2O_7 to the permanganates.

The preparation of these oxides in a pure state is a matter of some difficulty.

MnO is only prepared by the oxalate method.

Mn_2O_3 is found as the mineral *braunite.*

Mn_3O_4 is obtained by igniting very strongly any of the other oxides. Also as the mineral *manganite.*

MnO_2 is obtained in the hydrated state as H_2MnO_3 by the action of any oxidising agent (*e.g.* bromine water) on precipitated manganese hydroxide.

Mn_2O_7 is got as an unstable oil by cautiously adding strong sulphuric acid to potassium permanganate crystals, and keeping the mixture cool.

1. *The equivalent of manganese.*

The equivalent of manganese is not easy to find by a simple method, except by the analysis of the chloride $MnCl_2,4H_2O$. The percentage of water of crystallisation must be known, or else the anhydrous salt obtained by warming pure manganous carbonate in a stream of pure dry hydrochloric acid gas.

Some properties of manganous hydroxide.

2. Try the actions of caustic soda solution on a solution of a manganous salt. A white precipitate is formed. Divide into several portions, and—

(*a*) Shake up with air.

(*b*), (*c*), (*d*), etc. Add various oxidising agents, such as chlorine or bromine water, hydrogen peroxide, hypochlorites, etc. In each case filter, wash, and test the product with—

(*a*) Strong hot hydrochloric acid.

(*b*) Hot dilute nitric acid. Does any dissolve?

N.B.—Care should be taken that oxidation is *complete*, or test (*b*) would be misleading.

Hence what oxide has been formed by the oxidation of the hydroxide $Mn(OH)_2$? (1 hr.)

Compare the recovery of manganese dioxide in the "Weldon" process for making chlorine.

3. Compare the action of ammonium hydroxide on a manganous salt—

(*a*) Without previous addition of ammonium chloride.

Filter quickly and test the filtrate for manganese (bromine water).

(*b*) *First* adding ammonium chloride. Any precipitate? Stand aside for some time, and shake. Does anything worthy of note occur? Explain, in the light of Problem (1) and (2), how it is that in spite of adding ammonium chloride, some manganese always comes down in Group III. A in qualitative analysis, if it is present. ($\frac{1}{2}$ hr.)

4. *Action of nitric acid on the oxides of manganese.*

Try the action of excess of hot dilute nitric acid on the oxides of manganese, Mn_2O_3, Mn_3O_4 and MnO_2 (all very finely powdered). Find in each case whether any manganese goes into solution, and what is left undissolved. (Filter, wash, and test the *residue* with hot strong hydrochloric acid, the *filtrate* with caustic soda.) Compare also the action of each oxide with hot strong hydrochloric acid. From your results, state clearly the relation between all four oxides of manganese, and write their graphic formulæ. [*N.B.*—Manganous oxide, MnO, which is very difficult to obtain pure, would of course react with nitric acid in the usual manner of a basic oxide $MnO + 2HNO_3 = H_2O + Mn(NO_3)_2$.] Compare the constitutions of these three oxides of manganese with the corresponding oxides of lead, PbO, Pb_2O_3, Pb_3O_4 and PbO_2. See also the oxides of iron, FeO, Fe_2O_3 and Fe_3O_4. You should now be in a position to discriminate between the oxides (or hydroxides) of manganese, when you meet with them. (1 hr.)

5a. *Oxidation of manganese dioxide (manganous acid) to manganic acid, and the reactions of this acid.*

Fuse up some caustic potash, manganese dioxide, and a little potassium chlorate (Care!) in an iron or nickel dish. The manganese is thereby oxidised to the state MnO_3, giving the corresponding potassium salt K_2MnO_4 (potas-

sium manganate). This forms a green solution in water. Acidify some of the clear green solution (diluted considerably) with a weak acid (*e. g.* saturate with carbon dioxide), and boil. Note exactly what happens, and identify the precipitate and the filtrate.

Acidify some more of the green solution with any other acids, and note exactly what happens in each case. What has oxidised the manganate to permanganate? Give equations. (1 hr.)

5b. *The oxidising actions of permanganates in acid, neutral, and alkaline solutions.*

(i) *Acid.* To various reducing agents, such as ferrous salts, stannous chloride, etc., add excess of dilute sulphuric acid and then potassium permanganate solution. Find out—

(*a*) To what state the reducing agent has been oxidised.

(*b*) To what state the manganese has been reduced.

Hence deduce the equation for the oxidising action of permanganate in *acid* solution.

(ii) *Neutral.* Add alcohol dropwise to some hot neutral potassium permanganate solution. When the reduction seems complete (by disappearance of the purple colour) find out what the precipitate is; also whether any manganese is left in solution in any form. Hence give the equation for oxidation by permanganate in neutral solution.

(iii) *Alkaline.* Add some soda or potash to some permanganate solution, and add this solution slowly to a hot solution of sodium citrate (mild reducing agent). How far is the permanganate reduced? Compare other reducing agents, such as sodium tartrate. Is the action always the same?

6. *Action of a permanganate on potassium iodide.*

To 50 grams of pure potassium permanganate in a litre of hot water add a *strong* solution of 25 grams of potassium

iodide. Heat for some time on a water-bath, and if the pink colour of the permanganate has not gone, drop alcohol in carefully till it does. More iodide might be added, but excess is to be avoided. Hence the use of alcohol. *Test the liquid with litmus.* Neutralise exactly with acetic acid, filter, identify the precipitate (*i. e.* find out how far the permanganate has been reduced). Obtain crystals from the filtrate, and identify them, thus explaining what has become of the iodine.

Hence try and write an equation.

Compare the action of permanganate on potassium iodide solution to which (*a*) dilute sulphuric acid, (*b*) hydrochloric acid has first been added. (Test-tube experiments will suffice here.) Give equations.

7. *Oxidation of manganous manganese in acid solution.*

To a solution of a few grams of manganous sulphate or chloride add several cubic centimetres of a strong solution of sodium acetate. Now conduct chlorine into the mixture. *Avoiding excess of chlorine*, compare the reaction of the solution to litmus before and after passing chlorine in. Filter, and identify the precipitate. Compare with a similar experiment on chromium. (See Problem 7 under Chromium.)

Give an equation on similar lines. What is the function of the sodium acetate? Try the action of chlorine on the manganous salt *without* the previous addition of acetate. (1 hr.)

8. *Further investigation of the oxidation of manganous compounds in acid solution.*

To a hot solution of manganous sulphate add some permanganate solution gradually, till the last drop just gives a permanent pink. (Allow precipitate to settle.) Test the reaction of the liquid. It is strongly acid. *Nearly* neutralise with caustic soda, but keep just on the

acid side. Filter and wash. Identify the precipitate as nearly as you can by testing whether hot dilute nitric acid dissolves any manganese out of it, and what it leaves undissolved.

Now to a further quantity of manganous sulphate solution add excess of a strong solution of zinc sulphate, and treat exactly as before, *i.e.* with permanganate solution (hot); test the resulting liquid with litmus; approximately neutralise it (but not quite), filter, wash well, and identify the precipitate by treating with—

(*a*) Hot dilute nitric acid. What dissolves and what is left?

(*b*) Hot concentrated hydrochloric acid.

How do you think the presence of the zinc sulphate affects matters? Is the manganese completely oxidised this time? Can you, from your results, draw up a scheme for the volumetric estimation of manganese? (1½ hrs.)

9. Experiment 4 under Chromium may be done now if it has not been previously performed.

TRANSITIONAL ELEMENTS: IRON, NICKEL, COBALT.

IRON. Fe = 55·8.

Equivalents 27·9 *and* 18·6. *Atom therefore di- and trivalent.*

The oxides of iron are—

Ferrous oxide, FeO, basic and unstable.

Ferric oxide, Fe_2O_3, basic and stable (the mineral *haematite*).

Magnetic oxide, Fe_3O_4 (the mineral *magnetite*).

Salts corresponding to an unknown acid anhydride FeO_3 are also known.

E.g. potassium and barium ferrates have been isolated, and have the respective formulæ K_2FeO_4, $BaFeO_4$.

Ferrous oxide, FeO, is prepared by the oxalate method (see p. 11) owing to its ready oxidisability. It is at once sealed up in an atmosphere of carbon dioxide.

Ferric oxide, Fe_2O_3, is got by the general methods.

Magnetic oxide, Fe_3O_4, is the oxide obtained by burning iron in oxygen. (Also see below.)

1. The equivalent of ferrous iron is found (*a*) by the syphon-bottle method, using hot dilute hydrochloric acid; (*b*) by the substitution method (see p. 25).

The equivalent of ferric iron is found by the nitrate method. Ignition of ferric nitrate leaves Fe_2O_3.

2. *Distinctions between ferrous and ferric salts.*

Try the action on both ferrous and ferric salt solutions of the following solutions—

Caustic soda, ammonia, potassium ferrocyanide, potassium ferricyanide, potassium thiocyanate. From results state clearly—

(*a*) How to distinguish between a ferrous and a ferric salt.

(*b*) How to detect both ferrous and ferric salts when *mixed*.

N.B.—*Freshly made* ferrous sulphate solution is essential.

3. *Reduction of ferric salts.*

Try the action of the following reducing agents on ferric salts—

(*a*) Nascent hydrogen (zinc and dilute sulphuric acid).

(*b*) Sulphurous acid solution.

(*c*) Stannous chloride solution.

In each case see whether the ferric salts have been completely reduced. Also try the action of the following oxidising agents on ferrous salts—

(*a*) Chlorine water.

(*b*) Bromine water.

(*c*) Hypochlorites.

(*d*) Concentrated nitric acid and heat.

(*e*) Hydrogen peroxide.

(*f*) Dilute sulphuric acid followed by permanganate solution.

(*g*) Dilute sulphuric acid followed by potassium dichromate solution.

In each case give equations. From your results state clearly which is the most convenient reducing agent for ferric salts in the titration of iron by standard dichromate.

4. *Oxidation of ferrous hydroxide.*

(*a*) To a solution of ferrous sulphate add caustic soda and shake with air for some time. Compare with a similar experiment under Manganese.

(*b*) To a solution of a ferric salt add caustic soda.

(*c*) Now dissolve some of the oxide Fe_3O_4 in some hot concentrated hydrochloric acid, and test the solution with caustic soda. Also test it for both ferrous and ferric chlorides.

From your results what would you say was the relation between the three known oxides of iron? Confirm by taking a solution of ferrous sulphate, oxidising exactly two-thirds to ferric sulphate, and getting rid of excess of the oxidizing agent (hence use bromine, getting rid of excess by boiling). Now mix cold with the remaining one-third of ferrous sulphate, and compare the reactions of this solution with those of the solution of the oxide Fe_3O_4 in hydrochloric acid.

Hence devise a method for preparing Fe_3O_4. [Also try passing steam over red-hot iron nails, and burning iron wire in oxygen.]

5. *Oxidation of ferric iron.*

To about 100 c.c. of a fairly strong solution of potash

add 2 or 3 c.c of ferric chloride solution. Through the suspension of ferric hydrate, $Fe(OH)_3$, in excess of potash thus obtained, lead chlorine gas for some time. Arrangements should be made to prevent excess of chlorine from escaping into the room. After about half-an-hour a purple solution should be obtained. Find out as much as you can about the properties of this solution (Do not forget that it will also contain much potassium hypochlorite, $KClO$.)

6. In a small hard-glass flask of about 100 c.c. capacity put a mixture of fine iron filings or "ferrum redactum" (one part) and saltpetre (two parts), and heat strongly till the action starts. [*N.B.*—The flask should be clamped above an iron tray to prevent damage to the bench.] When cold, break the flask and extract the mass with several successive *small* quantities of ice-water, filtering through *asbestos or glass-wool.* Find out as much as you can of the properties of this solution.

One-half of it may be precipitated by adding barium chloride solution, and the precipitate filtered, washed with water, alcohol and ether, and dried at the ordinary temperature. The action of heat on this barium salt should be tried.

What do you think is the state of oxidation of the iron in these experiments (5 and 6)?

7. *Action of heat on ferrous sulphate crystals.*

Find out as much as you can about the action of heat (gentle at first, afterwards strong) on ferrous sulphate crystals. Identify as many of the products of the reaction as you can, also what is left. Write an equation, showing the various stages as far as possible.

8. Find the action, on a gently heated solution of ferric chloride, of the following substances—

The carbonates of barium, magnesium, zinc, manganese, copper. (The *precipitated* carbonates to be used.)

The hydroxide and oxide of copper.

The oxides of magnesium and zinc.

The experiments should be done in test-tubes, which may be heated in a vessel of boiling water. After heating for ten minutes or so, filter, and test the filtrate for (*a*) iron, (*b*) the metal added. Also test the precipitate for iron.

To find out in what state the iron exists in the precipitate, try the action of hot sodium carbonate solution on hot ferric chloride, and also of NaOH on ferric chloride. The reactions are comparable in every way. Does ferric carbonate exist, do you think? What is the immense practical importance of the above reactions. (45 mins.)

9. Find the action of gentle heat (250° C.) on crystallised ferric chloride. What is evolved? Is the product soluble in water? What does it largely consist of?

From your results to 7 and 8 devise a general method for purifying salts of the divalent metals from iron impurities. Remember that originally the source of all salts is some mineral, and that iron is practically omnipresent in minerals.

10. *Preparation of pure manganous chloride from pyrolusite.*

From commercial manganese dioxide, which contains *large* quantities of ferric oxide, prepare a quantity of *pure* manganous chloride. The method used must be devised on the results of 7 and 8, and *no other source* of manganese is to be used throughout.

N.B.—The residues obtained from the preparation of chlorine by the action of manganese dioxide on strong hydrochloric acid may be used as the starting-point.

11. *Purification of copper sulphate from ferrous sulphate.*

Prepare, from the crudest copper sulphate obtainable, a

pure crystalline specimen of copper sulphate. Remember that the chief impurity in copper sulphate is ferr*ous* sulphate. (1½ hrs.)

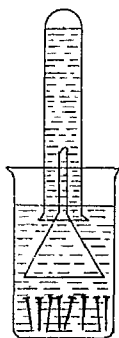
12. From crude granulated zinc, prepare a *pure* specimen of zinc sulphate. (1½ hrs.)

13. *An experiment on the rusting of iron.*

(*a*) Prepare a strong solution of carbonic acid in boiled (air-free) tap-water. Fill a beaker with this, and pack loosely at the bottom some clean bright iron nails. Cover with an inverted funnel, and over the funnel invert a test-tube filled with the same air-free carbonic acid as the beaker. Arrangements must now be made to keep it out of contact with air for at least a week. It may be put under a large bell-jar which stands on a greased glass-plate, and which is filled with carbon dioxide after the apparatus is inside.

After the lapse of a week or more, test the solution for

iron, see whether rusting has occurred, and try to find out what you can about any gas in the test tube.

FIG. 11.

(*b*) Prepare another experiment thus: Take an *air-free* solution of carbonic acid, fill a gas-jar with it, put some bright nails at the bottom as before, and cover them with a piece of filter-paper. Leave the whole exposed freely to the air for some days, and note *each day* what is happening. From your results to (*a*) and (*b*) explain how iron rusts.

14. *An experiment to explain the rusting of tin-plate and the non-rusting of galvanised iron.*

Tin-plate is iron coated with tin; galvanised iron is coated with zinc. Hence when tin-plate gets scratched and the iron exposed, we have, when it is wetted by rain, an

iron-tin electric element in a solution of carbonic acid. Similarly with galvanised iron, we get a zinc-iron element in carbonic acid. To imitate these conditions proceed thus—

Prepare a solution of carbonic acid and add a very small pinch of salt. This is to reproduce a sample of surface-water as nearly as possible.

Obtain two small rectangular glass cells, such as are used to set up a simple cell in elementary electricity. Fill with the artificial surface-water, and put in one, as shown in Fig. 12, a plate of iron and a plate of tin. Connect through a small sensitive galvanoscope * of low resistance and note which way the current flows (compare the direction of deflection with that produced by a Leclanché cell). Remove the galvanoscope, and complete the circuit by a copper wire. Leave overnight, or longer.

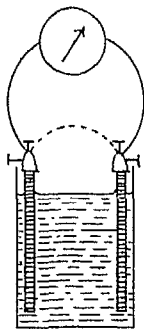



FIG. 12.

Repeat with the second cell, using a *zinc* plate instead of a tin one. Note direction of current as before, then short-circuit the cell and leave overnight.

From your results try and explain what you would expect to find on examining the cells after a few weeks. Now explain why galvanised iron does not rust, and why tin-plate, when once scratched in any way, rusts more quickly than ordinary sheet-iron.

NICKEL, Ni = 58·7 AND COBALT, Co = 59.

Equivalent of nickel = 29·35; *of cobalt* 29·5. *Atoms there-*

* A suitable galvanometer for this experiment is the small wedge-shaped instrument sold by W. G. Pye & Co.

fore divalent. Cobalt also has an equivalent 19·67, *being trivalent in these compounds. Nickel also is sometimes trivalent.*

The oxides of nickel and cobalt are—

Nickelous and cobaltous, NiO and CoO.

Nickelic and cobaltic, Ni_2O_3 and Co_2O_3.

The former is a peroxide, the latter more of a basic oxide, though in some of its reactions it behaves like a peroxide.

1. Both the equivalents of each metal can be found by reducing the corresponding oxide in hydrogen.

The Oxides and Oxidation of Nickel and Cobalt.

2. Ignite gently some nickelous nitrate, till no more nitrous fumes come off. Identify the residue by (1) treating with hot strong hydrochloric acid; (2) confirming by finding the percentage composition of the oxide by reduction in hydrogen. Repeat with cobaltous nitrate.

3. Find the action of caustic soda solution on both nickelous and cobaltous salts. Add the soda dropwise till in excess, and note everything that happens. Divide each solution so obtained into several parts and treat one portion of *each* as follows—

(*a*) Shake up well with air.

(*b*), (*c*), (*d*), etc. Treat with various oxidising agents, such as chlorine water, bromine water, hydrogen peroxide, etc. What happens in each case? Give equations.

4. Compare the action of potassium cyanide solution, added dropwise, on both nickelous and cobaltous salts, using equal volumes of equivalent solutions, and comparing roughly the volume of cyanide required by each. Boil a portion of each solution thus obtained. Does anything worthy of note occur? Test with litmus. Add caustic

soda to each of the boiled solutions after cooling. What happens?

To the other portion of each solution obtained after the addition of the cyanide, add caustic soda followed by chlorine or bromine water. Explain the difference in the reactions, and hence devise a separation of nickel from cobalt. (¾ hr.)

5. To a solution of cobalt *acetate* in acetic acid add excess of potassium nitrite solution. Warm, and stand aside for a short time, filter, and wash the precipitate with cold water, and identify it. Find out what is the state of oxidation of the cobalt. (1 hr.)

6. To solutions of nickel and cobalt chlorides add in the cold a little precipitated barium carbonate, and then bromine water dropwise. Explain the actions, if any, noting differences in the behaviour of the two metals. From results, devise and carry out a separation of nickel from cobalt.

Putting together your results from these last five problems on the oxidation of nickel and cobalt compounds, which metal do you consider more resembles iron in its chemical behaviour? Remember that all three elements come in the first lot of "transitional elements" in the periodic table, and that the atomic weight of nickel is between those of iron and cobalt.

7. *The carbonates of nickel and cobalt.*

Find out whether the normal carbonates of these metals can exist, or whether they are only basic carbonates.

8. *Preparation of a double cobalt salt.*

To a solution of cobalt *chloride* add some strong microcosmic salt solution. *Just* clear the precipitate with dilute hydrochloric acid. Boil, remove the flame, and carefully add ammonia till the precipitate first formed *just* redissolves. Allow to cool slowly, with occasional shaking. Filter off

the purple precipitate, wash it with ammonia, and dry at 100° C. Examine a little suspended in a drop of ammonia, under the microscope. Of what well-known crystalline substance does it remind you? Identify it by qualitative analysis, and find the action of heat on it.

PART III

PROBLEMS IN VOLUMETRIC ANALYSIS

IT is assumed that the student has some knowledge of the standardisation and use of the following solutions: standard acids and alkalis, permanganate, dichromate, silver nitrate, and iodine and thiosulphate solutions.

The following problems comprise a graduated course of analyses with the aid of the above solutions.

A. USE OF ACIDS AND ALKALIS

1. Compare the neutralising power for acids of the given substance before and after ignition.

Method.—Find the volume of N acid that a weighed amount will neutralise, and calculate for 1 gram.

Meanwhile another portion has been ignited. Find the volume of N acid that 1 gram of the residue will neutralise. (1¼ hrs.)

2. Find, by volumetric methods, the solubility in water, at the room temperature, of the following substances: (i) slaked lime; (ii) barium hydrate; (iii) anhydrous sodium carbonate; (iv) oxalic acid; (v) borax. (45 mins. each should be ample.)

Indicators to be used are methyl orange for iii. and v.; phenol phthalein for rest. Standard solutions of suitable strength to be chosen for each by the student.

3. Find the strength of the given solution of ammonium chloride (grams of NH_4Cl per litre), given N caustic soda and N acid. (¾ hr.)

4. The given crystals have the formula $Na_2CO_3xH_2O$. Given N acid, find x. ($\frac{1}{2}$ hr.)

5. Find the strength of the given solution of barium chloride (grams of $BaCl_2$ per litre), given N sodium carbonate and N acid. ($\frac{1}{2}$ hr.)

6. Find the strength of the given solution of copper sulphate (grams of $CuSO_4$ per litre), given N caustic soda and N acid. ($\frac{1}{2}$ hr.)

7. Given N caustic soda and N acid, find the percentage weight of copper in blue vitriol crystals ($CuSO_4 5H_2O$). ($\frac{3}{4}$ hr.)

8. Given $\frac{N}{25}$ acid, some lime-water, and a winchester quart bottle, find the percentage by *volume* of carbon dioxide in the laboratory air. (1 hr.)

9. Find, by a volumetric method, the vapour density of hydrochloric acid gas.

Method.—Collect some in a vessel of known volume (about 100 c.c.). A wide tube, with stopcock at each end, is suitable. The volume can be found by running in water from a burette. Absorb the gas in water, make up to 250 c.c., and titrate 50 c.c. at a time with $\frac{N}{10}$ alkali. Hence the *weight* of the gas collected can be found. The volume is known, hence the vapour density.

N.B.—*As it is almost impossible to get rid of the last traces of air from the tube in which the gas is collected, this must be allowed for. How?*

($1\frac{1}{2}$ hrs., including setting up the apparatus, should be long enough.)

10. Find the equivalent of zinc, given N sulphuric acid and N alkali. (45 mins.)

11. Given N acid and N caustic soda, find the ratio of the equivalents of zinc and magnesium. (1 hr.)

12. The given powder is either calcium or barium carbonate, or a mixture of the two. Given N acid and N caustic soda, find which it is. If a mixture, calculate from your results the percentage weight of each carbonate in the mixture. ($1\frac{1}{4}$ hrs.)

13. The molecular weight of the acid supplied is given. Using N alkali, find (*a*) its equivalent weight; (*b*) its basicity. ($\frac{1}{2}$ hr.)

14. You are given a solution of 10 grams of a metallic oxide in 1 litre of N sulphuric acid. Find the percentage composition of the dissolved oxide. Solutions required to be asked for. ($\frac{3}{4}$ hr.)

15 Find out as much as you can, by qualitative and volumetric analysis, about the composition of the salt supplied. A solution of the salt containing 1 gram in 100 c.c. of solution is also supplied. (2 hrs. should be ample.)

16. Assuming the percentage composition of water, prove that the law of reciprocal proportions holds for the elements zinc, hydrogen and oxygen, thus—

(*a*) Find, by a volumetric method, the weight of zinc that displaces 1 gram of hydrogen.

(*b*) Find, by a volumetric method, the percentage composition of zinc oxide (pure ZnO supplied). See Problem 14. (2 hrs.)

17. The solution supplied contains both ammonium and barium chlorides. Calculate the weights of each in a litre of solution. Standard solutions required to be asked for. Acids and alkalis only. (1 hr.)

18. The given solution contains both hydrochloric and sulphuric acids. Calculate the weights of each per litre of solution. Solutions required to be asked for. (1 hr.)

19. Devise a method for standardising acids by means of pure recrystallised borax ($Na_2B_4O_7, 10H_2O$). Try to carry it out. What precautions do you find it necessary to observe? *What indicator will you use, and why?*

N.B.—Borax reacts as alkaline to indicators as does sodium carbonate, and free boric acid affects indicators to about the same extent as carbonic acid does. Providing the correct indicator is chosen, the end point is just as sharp as when sodium carbonate is being titrated. (1 hr.)

B. USE OF PERMANGANATE.

Determination of iron in various substances.

1. Find the percentage of iron in the substance supplied.

2. Find the percentage of iron in iron alum.

3. The given solution contains both ferrous and ferric iron. Find the weight of each per litre.

Determination of oxalic acid.

4. Find the weight of oxalic acid ($H_2C_2O_4$) per litre of the given solution. (35 mins.)

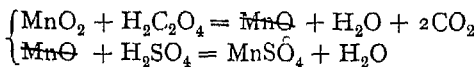
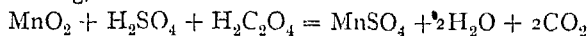
5. The composition of the given crystals is $K_2C_2O_4xH_2O$. Find x. (45 mins.)

6. Estimate the percentage of calcium in pure calcium carbonate (Iceland spar) by turning it to the oxalate and estimating the C_2O_4. (Assume the formula of calcium oxalate.) ($1\frac{1}{4}$ hrs.)

7. Find the percentage of manganese dioxide in some pyrolusite, by taking advantage of the fact that in sulphuric acid solution manganese dioxide oxidises oxalic acid, thus—

$$\begin{cases} MnO_2 + H_2C_2O_4 = MnO + H_2O + 2CO_2 \\ MnO + H_2SO_4 = MnSO_4 + H_2O \end{cases}$$

Adding, we have—

$MnO_2 + H_2SO_4 + H_2C_2O_4 = MnSO_4 + 2H_2O + 2CO_2$

Necessary precautions to take are—

(*a*) The pyrolusite must be *very finely powdered.*

(*b*) It is added to the oxalic and sulphuric acids and then heated, but not boiled. Care must be taken that the sulphuric acid used is not sufficiently hot and strong to decompose the oxalic acid in the usual way. Lead peroxide, PbO_2, may be estimated similarly. (1½ hrs.)

8. Find the weight of hydrogen peroxide in 1 litre of the given solution. Also find what volume of oxygen 100 c.c. of the solution will furnish. (½ hr.)

9. Given some $\frac{N}{10}$ oxalic acid, and a permanganate solution of unknown strength, find the number of grams of available oxygen in one litre of the permanganate solution. (35 mins.)

10. Find the weight of potassium nitrite in 100 grams of the commercial substance, using $\frac{N}{10}$ permanganate. Remember that nitrous *acid* is unstable, and will therefore be lost if the nitrite solution be acidified. (1 hr.)

11. Given a solution containing both oxalic and sulphuric acids, find the weight of each per litre of solution (1 hr.)

12. The given solution contains ferrous oxalate dissolved in excess of oxalic acid. Find the weight of each per litre of solution. (1½ hrs.)

C. ANALYSES BY MEANS OF $\frac{N}{10}$ POTASSIUM DICHROMATE.

1. Given some pure magnetic oxide of iron, Fe_3O_4, prove that its constitution is represented by FeO, Fe_2O_3, by dissolving in strong hydrochloric acid, with precautions against

oxidation, and comparing the ferrous with the ferric iron. (2 hrs.)

2. Given a sample of battery chromic acid, find the percentage of CrO_3 in it. Given a solution of ferrous sulphate such that 1 c.c. is oxidised by ·0008 gram of available oxygen. ($1\frac{1}{4}$ hrs.)

3. A ferrous salt is oxidised in acid solution by potassium chlorate, the chlorate being reduced to chloride. Write the equation, and given a $\frac{N}{5}$ solution of a ferrous salt, and $\frac{N}{10}$ potassium dichromate, find the percentage of potassium chlorate in a sample of the commercial salt. ($1\frac{1}{4}$ hrs.)

D. ANALYSES BY MEANS OF $\frac{N}{10}$ SILVER NITRATE.

This solution is very useful for determining the equivalent of a substance, by estimating the chlorine in the chloride. The equivalents of all metals whose chlorides are soluble in water and not hydrolised by it, and whose *chromates are also soluble in water*, can be found, providing that the pure chloride can be obtained. The latter stipulation is necessary, as potassium chromate is used as the indicator, the last drop of silver nitrate solution turning it a pink colour due to silver chromate, Ag_2CrO_4.

1. Find the equivalent of sodium, by finding the weight of sodium that combines with 35·5 grams of chlorine. *Pure NaCl must first be prepared.*

2. Find in a similar way the equivalent of potassium.

3. Find the percentage composition of sulphur monochloride, S_2Cl_2, by first preparing and purifying the sulphur chloride by direct combination of the elements and redistillation. Nitric acid acts on it to produce sulphuric

and hydrochloric acids and free sulphur. The titration must be carried out in *neutral* solution.

N.B.—The vapour of sulphur chloride has a very irritating action on the eyes and throat.

(The actual preparation of the substances required for these three problems takes some time. The titration, however, only requires about half-an-hour.)

4. The given substance is either pure sodium chloride, pure potassium chloride, or a mixture of the two. Given $\frac{N}{10}$ silver nitrate, find which it is. If it is a mixture, calculate the percentage of each in the mixture. ($1\frac{1}{4}$ hrs.)

5. Given a solution containing both hydrochloric and sulphuric acids, find the weight of each per litre. ($1\frac{1}{4}$ hrs.)

6. The given solution contains sodium chloride and hydrochloric acid. Find the weight of each per litre. ($1\frac{1}{4}$ hrs.)

7. Find the equivalent of bromine, given that the equivalent of potassium is 39. ($\frac{3}{4}$ hr.)

8. Find the equivalent of iodine, given that the equivalent of potassium is 39. ($\frac{3}{4}$ hr.)

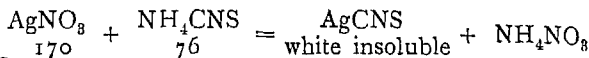
9. The given substance is a mixture of silver nitrate and potassium nitrate. Estimate the percentage of each, given $\frac{N}{10}$ sodium chloride solution. ($\frac{3}{4}$ hr.)

10. To a little dilute potassium cyanide solution add silver nitrate solution dropwise and explain what happens. From your observations devise and carry out a method for estimating potassium cyanide by means of $\frac{N}{10}$ silver nitrate. (2 hrs. should be ample.)

11. By means of the above reaction, estimate the percentages of NaCN and of KCN in the commercial "sodium potassium cyanide." ($1\frac{3}{4}$ hr.)

E. ANALYSES WITH $\frac{N}{10}$ AMMONIUM THIOCYANATE.

The reaction

$$\underset{170}{AgNO_3} + \underset{76}{NH_4CNS} = \underset{\text{white insoluble}}{AgCNS} + NH_4NO_3$$

is not appreciably affected by the presence of dilute nitric acid, and therefore silver can be estimated in *acid* solution by a standard thiocyanate solution. (Potassium thiocyanate will do just as well as the ammonium salt.) A ferric salt (iron alum) is used as indicator, the first excess of thiocyanate forming a blood-red coloration of $Fe(CNS)_3$, ferric thiocyanate.

N.B.—The end point colour is not very easy to determine without practice, as it is of necessity extremely dilute. A practical demonstration will teach the student better than any description.

1. Estimate the percentage of silver in a threepenny-bit. (1 hr. should be ample.)

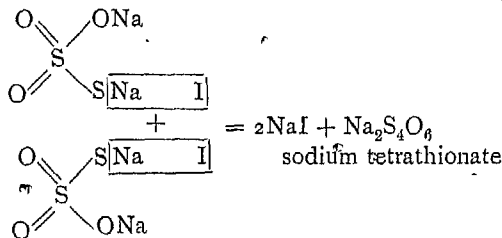
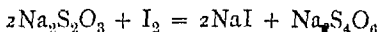
2. Find the percentage of bromine in hydrobromic acid, prepared by the action of water on phosphorus tribromide.

[For details of the preparation of hydrobromic acid see any book on Inorganic Chemistry.] (2 hrs.)

F. ANALYSES WITH $\frac{N}{10}$ IODINE AND $\frac{N}{10}$ THIOSULPHATE.

The action between iodine and sodium thiosulphate is—

or briefly—

$$2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$$

The action being immediate, quantitative, and readily followed by change of colour (blue iodide of starch used for greater accuracy), we can estimate—

(*a*) Any substance that turns out iodine from potassium iodide.

(*b*) Any substance that is oxidised quantitatively by iodine.

N.B.—The equivalent of iodine being 127, a *decinormal* solution contains 12·7 grams of iodine per litre. Since only *one* of the sodium atoms in the molecule of thiosulphate reacts with iodine, the equivalent weight of thiosulphate *with regard to this particular reaction* is the same as its molecular weight, and the $\frac{N}{10}$ solution therefore will contain $\frac{Na_2S_2O_3,5H_2O}{10}$ per litre = 24·8 grams of *crystalline* thiosulphate per litre.

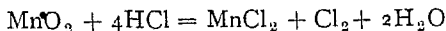
1. Find the strength in grams per litre of the chlorine water supplied. (½ hr.)

2. Find the solubility in water, at the room temperature, of (*a*) bromine; (*b*) iodine. (1½ hrs. for the two.)

3. Find the percentage of $Na_2SO_3,7H_2O$ in the given sodium sulphite crystals. (1 hr.)

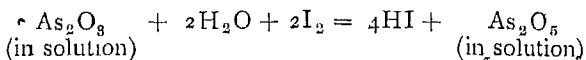
4. Find the weight of SO_2 per litre in the given solution of sulphurous acid. (½ hr.)

5. Find the percentage of manganese dioxide, MnO_2, in pyrolusite, by means of the reaction—

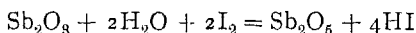
$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

Devise a simple apparatus to pass the evolved chlorine

through a solution of potassium iodide (which must be in excess) and titrate the iodine turned out. (2 hrs.)

6. Find the percentage of arsenious oxide, As_2O_3, in the commercial article, given that—

$$\underset{\text{(in solution)}}{As_2O_3} + 2H_2O + 2I_2 = 4HI + \underset{\text{(in solution)}}{As_2O_5}$$

The hydriodic acid must be neutralised as it is formed, or the reverse action will also take place. With what will you neutralise it? Remember that caustic soda and sodium carbonate both take up iodine. ($1\frac{1}{2}$ hrs.)

7. Find the percentage of antimony in tartar emetic, $K(SbO)\overline{Tar}$ (*i.e.* potassium antimonyl tartrate, the antimony being trivalent), given that—

$$Sb_2O_3 + 2H_2O + 2I_2 = Sb_2O_5 + 4HI$$

Hence one molecule of tartar emetic requires I_2 for its oxidation. As in Problem 6, the reverse action takes place unless the hydriodic acid is neutralised. ($1\frac{1}{2}$ hrs.)

Two convenient methods of standardising thiosulphate.

8. Write the equation for the oxidation of potassium iodide in *acid* solution (hydrochloric) by permanganate. Hence, given $\frac{N}{10}$ permanganate, standardise your thiosulphate. ($\frac{1}{2}$ hr.)

9. Repeat 8 with $\frac{N}{10}$ potassium dichromate.

10. Find the percentage of CrO_3 in "battery chromic acid," using the reaction observed in Problem 9.

11. *To find the action of a halogen on a silver salt in solution.*

Given $\frac{N}{10}$ silver *sulphate*, $\frac{N}{10}$ thiosulphate, and saturated bromine water, find the strength of the bromine water,

and add to a measured amount of the silver solution an exactly equivalent amount of the bromine water. Filter off the precipitate of silver bromide through glass-wool, and—

(*a*) Compare the oxidising power of the solution towards potassium iodide with that of the bromine water added.

(*b*) Analyse it qualitatively.

From your results, write out the action of bromine water on silver sulphate.

12. *The composition of bleaching powder.*

Set up an apparatus to pass dried chlorine over about 20 grams of pure dry slaked lime, cold. Find out what is formed, and estimate the total amount of chlorine absorbed per gram of the slaked lime, also the amount of "available" chlorine obtained on acidifying the product.

Is any calcium chloride formed, or calcium hypochlorite? (The chloride is soluble in absolute alcohol, the hypochlorite is not. Also the chloride is deliquescent.) What do you think is the formula of "bleaching powder"? Compare with the action of chlorine on alkalis in cold *solution*. (3 hrs.)

13. *Bromine bleaching powder.*

Try a similar experiment with bromine and slaked lime. (Avoid excess of bromine.) The vapour may be passed over the slaked lime by a *slow* stream of air (free from moisture and carbon dioxide) which bubbles through some bromine in a wash-bottle. Stop the action before any signs of a *red* compound begin to appear. Is there a "bromine bleaching powder," and is it, do you think, analogous to ordinary bleaching powder in constitution? (3 hrs.)

14. *Action of iodic on hydriodic acid.*

Given some sulphuric acid and some caustic soda solutions, both of unknown strength, some $\frac{N}{10}$ potassium iodate

(KIO_3,HIO_3), some $\frac{N}{10}$ thiosulphate, and some 10 per cent. potassium iodide solution. You are to find the strength of the sulphuric acid by the reaction : $HIO_3 + 5HI = 3H_2O + 3I_2$. (2 hrs.)

PART IV

APPENDIX

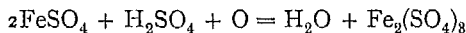
Notes on the various problems in Parts I, II and III.

Preparation of double salts.

Iron ammonium alum (p. 17).

(*b*) STARTING from ferric oxide Fe_2O_3 and ammonia. The formula of iron alum being $Fe_2(SO_4)_3,(NH_4)_2SO_4,24H_2O$, we note that three times as much SO_4 is in combination with Fe as with NH_4. Hence we put *three* boiling tubes full of dilute sulphuric acid into one basin, warm, and add precipitated Fe_2O_3 (not ignited) till no more will dissolve. *One* boiling tube full of the same acid is put into another basin, and neutralised with ammonia. The two solutions are filtered into the same dish, and crystallised in the usual way.

(*c*) Starting from $FeSO_4,7H_2O$, we want two molecules of it, plus one molecule of sulphuric acid, to form ferric sulphate, thus—

$$2FeSO_4 + H_2SO_4 + O = H_2O + Fe_2(SO_4)_3$$

The oxygen is supplied by strong nitric acid. One molecule of ammonium sulphate, $(NH_4)_2SO_4$, will be required to form the alum. Hence weigh out quantities of each ingredient in the proportions $2FeSO_4,7H_2O : H_2SO_4 : (NH_4)_2SO_4$. (Concentrated sulphuric acid is about 97 per cent. H_2SO_4.) Dissolve the ferrous salt in water, add the sulphuric acid, warm, and *carefully and slowly* add concentrated nitric acid in the proportion demanded by the equation $2HNO_3 \rightarrow H_2O + 2NO + 3O$. Remembering that $2FeSO_4$

requires 1 atom of oxygen, we see that a quantity of nitric acid proportional to $\frac{2HNO_3}{3}$ is required. (The strong acid may be regarded as about 60 per cent. HNO_3.) When the action is nearly over, a small portion may be tested for ferrous salt by means of potassium ferricyanide. When no more ferrous salt is indicated, evaporate the solution down nearly to dryness, (finally on a water-bath) take up in water, and add the solution of ammonium sulphate. Crystallise in the usual way.

Note on Chrome alum, p. 18.

Since the alums are isomorphous, a mixed solution containing different alums produces one kind of homogeneous crystal, containing both alums. Hence a mixture of aluminium alum and a little chrome alum produces amethyst crystals looking like iron alum. But when dissolved in water these give a green or violet solution (according to temperature), whilst iron alum gives a yellow solution.

If a crystal of chrome alum be left in a saturated solution of aluminium alum, the latter will be deposited on the chrome alum, and we shall have a colourless crystal with a violet "kernel."

HYDROGEN (p. 27).

Problem 1.—*Reducing power of electrolytic hydrogen.*

Electrolytic hydrogen will reduce various substances to their hydrides, and oxides (that will conduct) to their metals. Thus—

Arsenic → AsH_3.
Antimony → SbH_3.
Bismuth is unacted upon.
Palladium absorbs the hydrogen.
Lead peroxide, PbO_2, is reduced to spongy lead.
Lead sulphate, $PbSO_4$, ,, ,, ,, ,, etc.

Problem 2.—Percentage composition of water.

See any text-book of Chemistry. The hydrogen is best generated from zinc and dilute hydrochloric acid, scrubbed with glass-wool, washed with alkali, dried with concentrated H_2SO_4, and passed over a weighed quantity of red-hot copper oxide, the water being collected in a calcium chloride tube, this being protected from moisture in the air by a guard-tube containing calcium chloride.

Problem 3.—Weight of a litre of hydrogen.

Find the weight of hydrogen evolved when a known weight of magnesium is dissolved in dilute sulphuric acid. Use one of the many apparatus designed for this purpose, that of Fresenius being the simplest and the best. (See under CO_2 in carbonates, p. 138.) Then, by means of the syphon-bottle method, find the *volume* of hydrogen evolved by the *same weight* of magnesium. This gives us the weight of a known volume of hydrogen. Hence the weight of a litre.

Problem 4.—Heat of solution of water of crystallisation.

Whilst you are finding the heat of solution of the hydrated salt, a portion should be heated to 200° C. in a platinum crucible, and the dehydrated salt ground finely. In every case grind the substance finely. A delicate thermometer will be required. Use molecular proportions of the hydrated and anhydrous salts in the same weight of water, and add them gradually to the water, stirring well all the time. Employ any of the well-known methods of correction for loss of heat, and if the solution is *dilute*, its specific heat may be taken as 1. Otherwise the specific heat of the solution must be found afterwards.

The heat of solution of one gram of water of crystallisation will be found to be *negative*, and to approximate in most cases to 79, *i.e.* to the *latent heat of fusion of one gram of ice*. This is what might perhaps be expected.

Problem 5.—*Specific gravity of water of crystallisation.*

Any of the methods for finding the specific gravity of a powder may be used. *E.g.* by the specific gravity bottle, using a liquid whose density is accurately known, in which the substance is insoluble. As the substance is finely powdered, it must be put under the air-pump on being dropped into the liquid, to extract any air-bubbles it may hold. (These are generally very numerous, as the air-pump shows.)

You will find from your results—

That the volume of the hydrated salt is equal to the volume of its water of crystallisation in the state of ice. Hence the molecules of the salt must be packed in the spaces between the molecules of its water of hydration.

SODIUM (p. 29).

Problem 1.

Sufficient details for finding the equivalent are given with the problem.

Problem 2.—*Reduction of potassium chlorate by sodium amalgam.*

If the time-E.M.F. curve shows any considerable fall, it means that polarisation is taking place. On the other hand, if no polarisation is taking place, then the hydrogen which would otherwise be liberated at the surface of the plate of metal is being oxidised by the chlorate. Hence

we should expect to find that the *less* the polarisation observed, the *greater* the amount of reduction. The E.M.F. of the element has nothing to do with the amount of reduction; it is the *back* E.M.F. (polarisation E.M.F.) that counts.

The *actual* amount of reduction need not be found. All that is required is a comparison. Hence the volumes of $\frac{N}{100}$ silver nitrate used, which are proportional to the reduction, can be taken. It is, of course, obvious that the same volume of the same solution of chlorate must be used for each metal, and that the same volume be taken for titration. The object of short-circuiting the cell is that owing to the high resistance of the voltmeter, such a small current passes that the amount of reduction would be inappreciable.

POTASSIUM (p. 30).

Problem 1.

Sufficient details are given with the problem.

Problem 2.—*Catalytic decomposition of potassium chlorate.*

To compare their efficiency, it is obvious that we must observe the following conditions—

(*a*) Each must be heated to the same extent, and compared with the same weight of chlorate heated *alone* under the same conditions.

(*b*) The decomposition of the chlorate must in *no* case be *complete*, or the efficiencies will all come out alike. Hence we must heat *gently* for quite a short time.

Take four fairly large crucibles. Into each weigh out about 5 grams of the powdered chlorate. Take the same weight in each case. Mix, in three of the crucibles, molecular proportions of the catalysts by means of a stout platinum wire.

Now heat each crucible, under precisely the same conditions, for the same time. For this, a bunsen burner should be turned down so that the flame *just touches* the bottom of the crucible. Each crucible is then heated in turn, and whilst it is being weighed the next one is heated. In this way the four can be done in about 45 minutes. Five minutes each will be found sufficient. In each case calculate the percentage loss of weight; if it is larger than that of the chlorate heated alone, then the substance has assisted, catalytically or otherwise.

In the case of the oxide Cr_2O_3, it will be observed that it has all gone to CrO_3 (potassium chromate). Does any chlorine come off? Test the reaction of the solution. Is it acid? From your results you should have no difficulty in making an equation.

The action of the silica seems to be purely catalytic; no potassium silicate will be found under the above conditions.

The action of ferric oxide will also probably appear to be catalytic, but under certain conditions one *may* get a little potassium ferrate formed (violet solution) indicating the formation and decomposition of the oxide FeO_3, just as in the case of chromic oxide. [For FeO_3 see under Iron.]

After the quantitative comparisons have been made, each crucible may be heated strongly, and any change in the catalyst noted.

Problem 3.—*Detection and estimation of chloride, chlorate and perchlorate of potassium.*

It will be found that potassium chlorate oxidises ferrous sulphate in acid solution, but that perchlorate does *not.* Hence to test for a chloride, chlorate and perchlorate in the presence of one another, proceed thus—

(*a*) Dissolve in water, acidify with dilute nitric acid, and add silver nitrate till no more precipitate falls. Filter. The precipitate is silver chloride, confirming chloride.

Warm the filtrate, and drop it into some warm ferrous sulphate solution containing excess of sulphuric acid. See that the reduction of the chlorate is complete by there being excess of ferr*ous* sulphate left (Ferricyanide test). Now test for a chloride with silver nitrate. A precipitate of silver chloride means that a chlorate has been reduced to chloride. Complete the precipitation of the chloride, and evaporate the filtrate dry. Ignite. Dissolve in water, filter, and again test for chloride. A precipitate means that perchlorate was present. Equations should be given for each reaction.

The estimation of each is carried out in an obvious way. First of all a weighed quantity of the mixture is dissolved in water, and the *chloride* chlorine in 25 c.c. estimated with $\frac{N}{10}$ silver nitrate. A further 25 c.c. is dropped into hot ferrous sulphate solution containing excess of sulphuric acid, and the total chlorine (representing *chloride* and *chlorate* chlorine) estimated by adding excess of $\frac{N}{10}$ silver nitrate and titrating the excess with $\frac{N}{10}$ thiocyanate (*q.v.*, p. 102). This, *minus* the chloride chlorine, gives the chlorate chlorine, and hence the chlorate. A further weighed portion is heated to redness, thus turning everything to potassium chloride. Now estimate the *total* chlorine with $\frac{N}{10}$ silver nitrate. This, *minus* the chloride and chlorate chlorine = the perchlorate chlorine, and hence the weight of potassium perchlorate.

COPPER (p. 31).

(i) *Determination of the equivalent of cupric copper.*

(*a*) Weigh into a clean porcelain basin about 2 grams of *clean* copper foil. Dissolve in the least possible quantity of strong nitric acid (added from a small pipette), keeping the basin covered with a clock-glass to prevent loss by spirting. Wash off, with the minimum of water from a wash-bottle, any solution that has got into the clock-glass. Evaporate dry on a water-bath, or VERY cautiously on a sand-bath. Finally heat on the sand-bath till the residue of copper nitrate has turned black, and finish off at a red heat over the naked flame. Weigh the residue of copper oxide, CuO, and calculate the amount of copper that combines with 8 grams of oxygen.

(*b*) Pass a stream of hydrogen, dried by bubbling through a small wash-bottle containing strong sulphuric acid, through a combustion tube containing a porcelain boat in which pure freshly ignited copper oxide has been weighed. When all the air has been swept out, heat the boat strongly for 15 to 20 minutes, allow to cool *in the stream of hydrogen*, and weigh the copper. The procedure with the red oxide will be similar, except of course that the red oxide must *not* be first ignited.

(*c*) A weighed amount of "spongy" copper is heated strongly for at least half-an-hour in an open basin, and is continually stirred with a stout iron wire that has been weighed with the basin. Unless stirred well the oxide formed will "cake" together and prevent complete oxidation. This is the least reliable method of the three.

(ii) *Equivalent of cuprous copper.*

(*a*) Procedure as in (i) (*b*).

(*b*) By synthesis of Cu_2S (cuprous sulphide).

Weigh a piece of clean copper foil (not more than

2 grams) into a Rose's crucible. (This is a crucible with a hole in the lid. See Fig. 13) Put in with it about the same weight of the best roll sulphur, and heat with a current of dry hydrogen passing through the crucible. This prevents any copper oxide being formed by oxidation of the sulphide. Cool in the hydrogen stream, add a further small piece of sulphur, and heat up again till all excess of sulphur has been expelled. Calculate the weight of copper that has combined with 16 grams of sulphur. Note that 16 is the equivalent of sulphur in H_2S, of which the substance prepared is the cuprous salt.

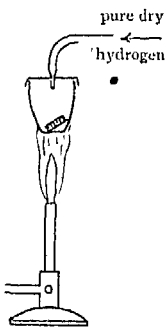
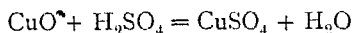
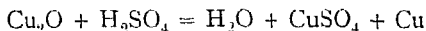



FIG. 13.

Problem 2.—*Action of sulphuric acid on the oxides of copper.*

On the black oxide the action is—

$$CuO + H_2SO_4 = CuSO_4 + H_2O$$

The action on the red oxide, Cu_2O, is to produce copper sulphate and free copper, thus—

$$Cu_2O + H_2SO_4 = H_2O + CuSO_4 + Cu$$

Method.—Treat the oxide in a boiling tube with hot dilute sulphuric acid. Filter, obtain crystals of copper sulphate from the filtrate, wash the residue of spongy copper on the filter with boiling water at least six times, and dry by spreading out the filter on a clock-glass over a basin of boiling water. Identify as copper by—

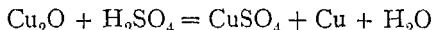
(1) Rubbing it hard in a mortar.

(2) Action of heat.

Any other methods that suggest themselves.

Problem 3.—*Quantitative confirmation of* (2).

According to the equation

$$Cu_2O + H_2SO_4 = CuSO_4 + Cu + H_2O$$

the weight of copper left over should be equal to the weight of copper in the copper sulphate formed. Hence treat some cuprous oxide, Cu_2O (which obviously need not be weighed), with excess of dilute sulphuric acid, and keep it hot for several minutes. Filter through a *weighed* filter, wash twice with hot water, and add the washings to the filtrate. Wash the residue further with boiling water till the filtrate is quite free from sulphuric acid (litmus). Then wash once with alcohol, once with ether, and dry in the steam oven. Weigh.

Displace the copper from the filtrate of copper sulphate by adding pure zinc foil until the blue colour has quite disappeared. Dissolve any excess of zinc in dilute sulphuric acid, filter through a weighed filter, and treat as above. The two amounts of copper should be equal in weight.

Problem 4.—*Action of hydrochloric acid on copper.*

(*a*) Boil some pure hydrochloric acid in a small flask for some minutes. Drop in a piece of clean copper foil, boil a minute or two longer, and quickly cork up with a rubber stopper. Set aside. No action should be observable even after several days, the copper remaining quite clean.

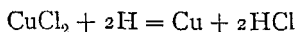
(*b*) Drop a piece of copper foil into some strong hydrochloric acid in a basin. After a short time, distinct evidence of the formation of cupric chloride, $CuCl_2$, should be noticed.

(*c*) Hang the copper foil in the flask by suspending it from, say, a hook of glass pushed through a rubber stopper.

Otherwise the experiment is the same as (*a*). No action should be observed, the copper remaining quite clean.

(*d*) Simply hang a piece of copper foil in a flask containing some strong hydrochloric acid. Evidence of the formation of cupric chloride should soon be noted.

Thus we see that copper is only acted on by hydrochloric acid if oxygen is present. This is probably accounted for by the fact that nascent hydrogen will reduce copper salts to copper, thus—

$$CuCl_2 + 2H = Cu + 2HCl$$

and that as nascent hydrogen would be produced *if* the action

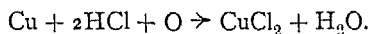
$$Cu + 2HCl = CuCl_2 + 2H$$

took place, it never does take place, for the nascent hydrogen given off by the action would be sufficient to reduce the chloride to copper again.

Hence the action

$$Cu + 2HCl \rightleftharpoons CuCl_2 + 2H$$

is reversible, but the reaction goes to the left so much more readily than to the right that practically no chloride is formed. If, however, air or oxygen be present, this takes up the nascent hydrogen, forming water, and so the reaction can go from left to right much more readily.

$$Cu + 2HCl + O \rightarrow CuCl_2 + H_2O.$$

Problem 5.—*The action of dilute hydrochloric acid on cuprous oxide.*

This is to form cuprous chloride, which is a white powder, insoluble in water, but soluble in strong hydrochloric acid, probably forming a complex acid of the formula $H_4Cu_2Cl_6$ ($Cu_2Cl_2 + 4HCl$).

This, however, is decomposed by water into its constituents $4HCl + Cu_2Cl_2$.

Hence with dilute hydrochloric acid, a certain amount of cuprous chloride, Cu_2Cl_2, is formed, which, being insoluble, coats the particles of oxide and prevents further action. If the hydrochloric acid is strong, however, this coating is dissolved off, and the acid $H_4Cu_2Cl_6$ is formed, the action thus being complete. On diluting the product, the cuprous chloride is obtained as a white precipitate. Hence the action

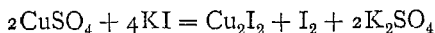
$$2HCl + Cu_2O \rightarrow H_2O + Cu_2Cl_2$$

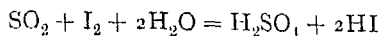
is the normal action of an acid on a base.

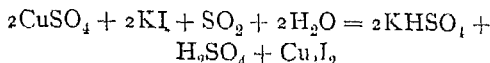
Problem 6.—Action of potassium iodide on copper sulphate.

On adding potassium iodide to copper sulphate solution we get a solution in which free iodine is at once recognised, and a precipitate falls, which after thorough washing is seen to be white. The action of hot strong sulphuric acid on this is to give iodine, together with reduction products of the sulphuric acid, showing it to be AN IODIDE. The action of soda is to give us the well-known orange-red cuprous hydroxide $Cu_2(OH)_2$, showing it to be a cupr*ous* salt.

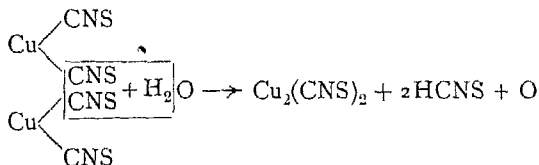
Hence we see that cupric iodide, which one would expect to be formed, is quite unstable, and immediately breaks up into $Cu_2I_2 + I_2$, thus—

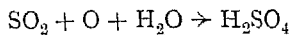
$$2CuSO_4 + 4KI = Cu_2I_2 + I_2 + 2K_2SO_4$$

The action is not quite complete, however. Some copper remains in solution. If SO_2 be present, however, this free iodine will be reduced back to HI in the usual way.

$$SO_2 + I_2 + 2H_2O = H_2SO_4 + 2HI$$

and the hydriodic acid produced then reacts with the copper sulphate like potassium iodide does. Hence in the presence of sulphur dioxide, only *one half* the amount of iodide is needed to precipitate the copper, and the precipitation of the copper will be *complete.* The full reaction is—

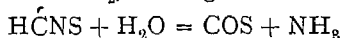
$$2CuSO_4 + 2KI + SO_2 + 2H_2O = 2KHSO_4 + H_2SO_4 + Cu_2I_2$$

Problem 7.—Action of thiocyanate on copper sulphate.

The action here is somewhat analogous to the one in the preceding problem. One would expect $Cu(CNS)_2$ to be produced, and so it is at first (black precipitate), but it gradually turns to the cupr*ous* salt, which is the more stable, thus—

$$Cu\begin{matrix}\diagup CNS \\ \diagdown \boxed{CNS} \end{matrix} \quad Cu\begin{matrix}\diagup \boxed{CNS} \\ \diagdown CNS\end{matrix} \;\; \boxed{CNS + CNS + H_2}O \rightarrow Cu_2(CNS)_2 + 2HCNS + O$$

If sulphur dioxide be present to take up this atom of oxygen, the change is much more rapid.

$$SO_2 + O + H_2O \rightarrow H_2SO_4$$

We note, in the course of the action, that on first mixing the two solutions, a black precipitate forms, which slowly turns lighter, and rapidly becomes white on adding sulphur dioxide solution. The white precipitate, on adding strong sulphuric acid, gives off carbon oxysulphide, COS, a gas which burns with a blue flame very much like that of

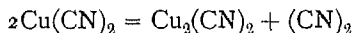
carbon monoxide, but is recognised by sulphur dioxide being produced as well as CO_2, showing it to be a thiocyanate.

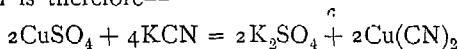
$$HCNS + H_2O = COS + NH_3$$

The NH_3, of course, is kept back by the acid.

NaOH gives orange-coloured $Cu_2(OH)_2$ when added to the precipitate, showing it to be a cupr*ous* salt.

Problem 8.—*Copper cyanide.*

Again the action is somewhat similar to those in the preceding problems. $Cu(CN)_2$ is unstable, and rapidly breaks up, thus—

$$2Cu(CN)_2 = Cu_2(CN)_2 + (CN)_2$$

The cyanogen is recognised by the beautiful characteristic flame with which it burns, whilst the white precipitate that forms gives carbon monoxide with concentrated sulphuric acid, showing it to be a cyanide, and cuprous hydrate, $Cu_2(OH)_2$, with soda, showing it to be a cuprous salt. The action is therefore—

$$2CuSO_4 + 4KCN = 2K_2SO_4 + 2Cu(CN)_2$$

and then $$2Cu(CN)_2 = Cu_2(CN)_2 + (CN)_2$$

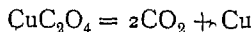
The action of more cyanide solution on this precipitate is to dissolve it, and form thereby a complex cyanide, thus—

$$Cu_2(CN)_2 + 6KCN = 2K_3Cu(CN)_4$$

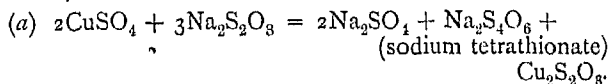
i. e. potassium cupr*o*cyanide.

Problem 9.—*Action of heat on copper oxalate.*

If copper oxalate is heated away from air, as, for instance, in a long narrow test-tube fitted with a cork carrying a couple of inches of narrow delivery tubing, metallic copper is left, and carbon dioxide is evolved, thus—

$$CuC_2O_4 = 2CO_2 + Cu$$

Problem 10.—*Action of sodium thiosulphate on copper sulphate.*

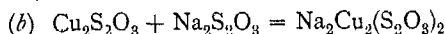
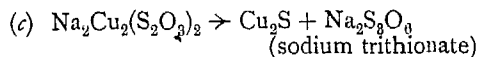
The precipitate will be identified as cupr*ous* sulphide, and *no* copper will be found in the filtrate. Note also that on adding the thiosulphate, no precipitate is formed, but the solution goes colourless. Putting this with the fact that cupr*ous* sulphide is precipitated, it would appear that the copper becomes reduced to the cuprous state, probably in solution, thus—

(*a*) $2CuSO_4 + 3Na_2S_2O_3 = 2Na_2SO_4 + Na_2S_4O_6 + Cu_2S_2O_3.$
(sodium tetrathionate)

cupr*ous* thiosulphate thus being formed at once.

This dissolves in excess of $Na_2S_2O_3$, forming a double salt (compare silver).

(*b*) $Cu_2S_2O_3 + Na_2S_2O_3 = Na_2Cu_2(S_2O_3)_2$

and on boiling

(*c*) $Na_2Cu_2(S_2O_3)_2 \rightarrow Cu_2S + Na_2S_3O_6$
(sodium trithionate)

With cadmium salts no such action takes place. Hence the separation of copper from cadmium by this method is obvious.

Problem 11.—*Decolorisation of copper sulphate solution by animal charcoal.*

The qualitative analysis of the *ash* from animal charcoal will supply the reason for the decolorisation of the copper sulphate.

SILVER (p. 35).

Problem 1.—*The equivalent of silver.*

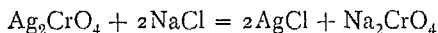
The equivalent is best found by dissolving a known weight of pure silver in the minimum quantity of half and

half nitric acid, taking precautions to prevent loss by spirting. The solution is diluted considerably with distilled water, and the silver is precipitated as silver chloride by adding dilute hydrochloric acid or a solution of sodium chloride till no further precipitate forms. Boil to make the precipitate go together. This precipitate is washed, dried, and weighed in the usual way. (For details see any book on Quantitative Analysis.) Calculate the weight of silver that combines with 35·5 grams of chlorine.

(The equivalent can also be found by the "substitution" method, for which see "Notes on Equivalents," p. 25.)

Problem 2.—Action of a soluble chloride on silver chromate.

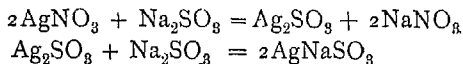
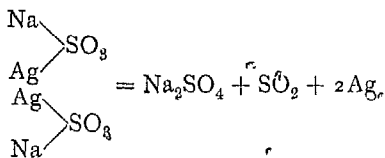
It will be found that as long as any chloride is left in solution, no precipitate of silver chromate, Ag_2CrO_4, is formed, for this reacts with a soluble chloride just like silver nitrate does.

$$Ag_2CrO_4 + 2NaCl = 2AgCl + Na_2CrO_4$$

Problem 3.—Reactions of some silver salts.

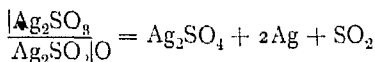
(*a*) Silver sulphite is precipitated, which is soluble in excess of the precipitant. As much should be required to dissolve the precipitate when completely formed as was required to form it. Thus—

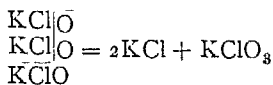
$$2AgNO_3 + Na_2SO_3 = Ag_2SO_3 + 2NaNO_3$$
$$Ag_2SO_3 + Na_2SO_3 = 2AgNaSO_3$$

On boiling this solution—

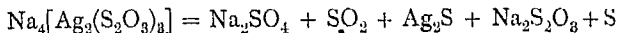
$$\left.\begin{matrix}Na \\ Ag\end{matrix}\right\rangle SO_3 \quad \left.\begin{matrix}Ag \\ Na\end{matrix}\right\rangle SO_3 = Na_2SO_4 + SO_2 + 2Ag.$$

Identify the precipitate as metallic silver, and test for SO_2 being evolved. Also test the filtrate for sulphate.

(*b*) If silver sulphite *alone* is heated to 100° C, part of the sulphite is oxidised at the expense of the other part, which is reduced to sulphur dioxide and metallic silver—

$$\frac{|Ag_2SO_3}{Ag_2SO_2|O} = Ag_2SO_4 + 2Ag + SO_2$$

Hence silver should be found in the *filtrate* as well as in the precipitate. Smell the sulphur dioxide evolved, and test the filtrate for a sulphate. (Use barium *nitrate*. Why?) Note the parallel case of the self-oxidation of the hypochlorites of NaClO or KClO. If a solution of either of these substances is boiled for some time, the hypochlorite is oxidised to chlorate by another portion, which is in turn reduced to chloride.

$$\begin{array}{l} KCl|O \\ KCl|O = 2KCl + KClO_3 \\ KClO \end{array}$$

Compare also the action of heat on sodium thiosulphate crystals, and on sodium sulphite crystals (under Sulphur, page 70).

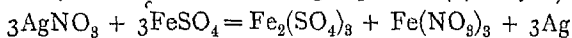
(*c*) $Ag_2S_2O_3$ is first produced, soluble, in more thiosulphate to form $Na_4[Ag_2(S_2O_3)_3]$. By boiling this solution, Ag_2S is precipitated, thus—

$$Na_4[Ag_2(S_2O_3)_3] = Na_2SO_4 + SO_2 + Ag_2S + Na_2S_2O_3 + S$$

Compare Copper, Problem 9.

Problem 4.—Action of ferrous sulphate on silver nitrate.

There is no action in the cold, but on boiling a precipitate forms which is recognised as metallic silver, and the ferrous

salt is oxidised to ferric, sometimes, especially with dilute solutions, a basic ferric salt being deposited (hydrolysis).

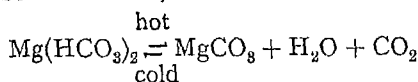
$$3AgNO_3 + 3FeSO_4 = Fe_2(SO_4)_3 + Fe(NO_3)_3 + 3Ag$$

MAGNESIUM (p. 36).

Problem 1.

Find the equivalent as directed. (For details see "Notes on Equivalents," p. 22).

Problem 2.—*Magnesium carbonate.*

Sodium carbonate precipitates the *normal* carbonate, not a basic carbonate, from solution, as if strong solutions be used, *no* carbon dioxide is evolved. It may otherwise be shown to be the normal carbonate in the usual way by estimation of the percentage of carbon dioxide by means of one of the many pieces of apparatus for this purpose. [Fresenius' is the best, owing to its simplicity.] The percentage of carbon dioxide should be that demanded by the formula $MgCO_3$. Sodium bicarbonate will in strong solutions give carbon dioxide and magnesium carbonate,—$MgCO_3$, *to a certain extent*, but in dilute solutions there will be little or no precipitate at all, magnesium bicarbonate being formed, which is soluble. If a precipitate forms, filter and boil the filtrate, when—

$$Mg(HCO_3)_2 \underset{\text{cold}}{\overset{\text{hot}}{\rightleftharpoons}} MgCO_3 + H_2O + CO_2$$

Thus the bicarbonate of magnesium is chemically like the bicarbonate of calcium, and is in fact always found with the latter in temporarily hard water.*

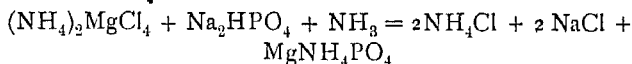
Problem 5.

The precipitate will be found to be a double phosphate of ammonium and magnesium containing water of crystal-

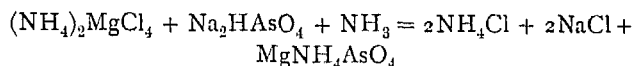
* With hot very dilute sodium carbonate, a certain amount of more

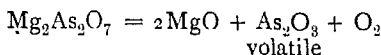
lisation. The actual formula is $MgNH_4PO_4,6H_2O$. On ignition, $2MgNH_4PO_4 = H_2O + Mg_2P_2O_7 + 2NH_3$.
pyrophosphate

Prove that a pyrophosphate has been formed. (See under Phosphorus, Problem 2.) The formation of the precipitate is as follows—

$$(NH_4)_2MgCl_4 + Na_2HPO_4 + NH_3 = 2NH_4Cl + 2NaCl + MgNH_4PO_4$$

Problem 4.

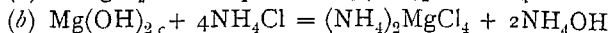
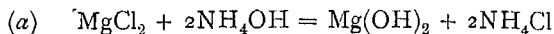
An exactly similar precipitate is formed to that in the previous problem, only that it contains arsenic instead of phosphorus. (Examine some of each under a microscope, whilst suspended in a drop of the liquor.)

$$(NH_4)_2MgCl_4 + Na_2HAsO_4 + NH_3 = 2NH_4Cl + 2NaCl + MgNH_4AsO_4$$

It crystallises, like the phosphate, with six molecules of water, and decomposes similarly on heating. If heated strongly, however, like other arsenates, oxygen will be evolved and the arsenate reduced to arsenite, from which As_2O_3 is volatile.

$$Mg_2As_2O_7 = 2MgO + \underset{\text{volatile}}{As_2O_3} + O_2$$

so that magnesium oxide will finally be left.

Problem 5.—*Precipitation of magnesium hydroxide by ammonia.*

With ammonia, a precipitate of magnesium hydroxide will be formed, but magnesium will remain in solution. If done quantitatively, as it should be done, one half of the magnesium will be found to remain in solution. This is owing to the formation of a double salt, magnesium ammonium chloride, which is stable to ammonium hydroxide.

(*a*) $MgCl_2 + 2NH_4OH = Mg(OH)_2 + 2NH_4Cl$
(*b*) $Mg(OH)_2 + 4NH_4Cl = (NH_4)_2MgCl_4 + 2NH_4OH$

Note that the amount of ammonium chloride formed in the first equation is just sufficient to dissolve one half of the magnesium hydroxide there formed according to (*b*).

The reason for adding ammonium chloride in Group III A in Qualitative Analysis is therefore clear. Since only half the magnesium would be precipitated as the hydroxide, $Mg(OH)_2$, it is better to suppress it altogether, otherwise it would come in two groups, III A and V. [Compare Zinc, Problem 4.]

Problem 6.—*Action of a hypoiodite on a magnesium salt.*

A dark-red precipitate is formed, which is probably $Mg(IO)_2$, magnesium hypoiodite, but it is hydrolysed by the water after standing for a short time, leaving the white hydroxide, $Mg(OH)_2$. Nevertheless, the action forms an interesting test for magnesium *in the absence of other bases except sodium and potassium*, as it is the only *coloured* salt of magnesium.

ZINC (p. 38).

Problem 1.—*The equivalent of zinc.*

For details, see "Notes on Equivalents," p. 22.

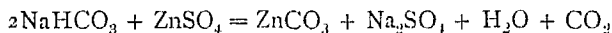
Problem 2.—*On the carbonates of zinc.*

Sodium carbonate precipitates a basic carbonate for—

(*a*) Carbon dioxide is evolved, even when the solutions are strong.

(*b*) The percentage of carbon dioxide in the precipitate is *less* than that required by the formula $ZnCO_3$. The actual composition of the basic carbonate varies with the

concentration and temperature of the solutions. The bicarbonate, however, does precipitate the normal carbonate, there being *no* bicarbonate of zinc. Prove this by adding sodium bicarbonate till no more precipitate falls, filtering, and boiling the filtrate. Also find the percentage of carbon dioxide in the dried precipitate.

$$2NaHCO_3 + ZnSO_4 = ZnCO_3 + Na_2SO_4 + H_2O + CO_2$$

Problem 3.—Action of nitric acid on zinc.

See under NITROGEN, Problem 3.

Problem 4.—On the precipitation of zinc by ammonia.

The actions are exactly similar to those with magnesium [for which see Problem 5 under Magnesium].

CADMIUM (p. 39).

Problem 1.—To find the equivalent.

Find the equivalent as directed. [For details see "Notes on Equivalents," p. 22.]

Problem 2.—The carbonates of cadmium.

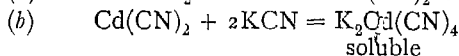
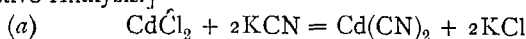
The actions are similar to those with zinc (Problem 2). On heating, $CdCO_3$ readily $\rightarrow$ CdO + CO_2.
(brown)

Problem 3.—Separation of cadmium from copper.

Cadmium cyanide is at first produced, a white precipitate, soluble in excess of KCN. From this solution, the only reagent that will precipitate the cadmium is H_2S. Compare the action of KCN on copper salts, and note that H_2S even will not precipitate the copper from potassium cupro-

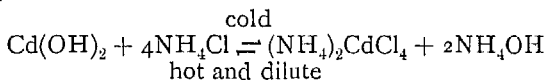
cyanide. [Hence the usual separation in Group II, Qualitative Analysis.]

(*a*) $CdCl_2 + 2KCN = Cd(CN)_2 + 2KCl$

(*b*) $Cd(CN)_2 + 2KCN = \underset{\text{soluble}}{K_2Cd(CN)_4}$

See also under Copper, Problems 8 and 10.

Problem 4.—*On the precipitation of cadmium by ammonia.*

The action is precisely similar to the corresponding actions with zinc and magnesium (see Magnesium, Problem 5), except that the complex salt $(NH_4)_2CdCl_4$ is less stable, and on diluting and boiling its solution, the reverse action comes into play and the hydroxide $Cd(OH)_2$ is precipitated, thus—

$$Cd(OH)_2 + 4NH_4Cl \underset{\text{hot and dilute}}{\overset{\text{cold}}{\rightleftharpoons}} (NH_4)_2CdCl_4 + 2NH_4OH$$

MERCURY (p. 39).

Problem 1.—*To find the equivalent.*

Sufficient details are given with the problem.

Problem 2.—*The carbonate of mercury.*

In the cases of mercuric nitrate and mercuric chloride, on adding sodium carbonate, *carbon dioxide will be evolved*, and a brown precipitate left. This must therefore be a *basic* carbonate. (Why not the oxide?) This *same* precipitate is formed by adding sodium bicarbonate to mercuric nitrate, and is therefore also a basic carbonate. Mercuric chloride and sodium bicarbonate do not react.

Mercuric cyanide will not give any reaction for mercury with ordinary reagents, except hydrogen sulphide.

When we compare the conductivities of equivalent solu-

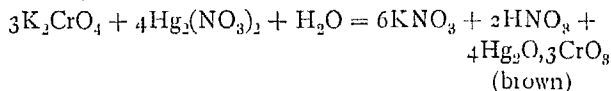
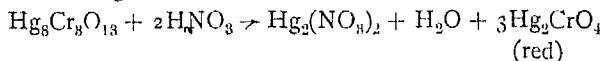
tions of these three salts, we find the conductivity of the cyanide is *much lower* than that of the other two, whilst that of the chloride is less than that of the nitrate. We conclude therefore that the two former are *not largely ionised* in aqueous solution, and hence the failure of the wet tests, *which are reactions for ions.* The cyanide is scarcely ionised at all, and will not give the usual wet tests for a cyanide.

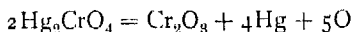
Problem 3.—*Mercurous chromate as a means of estimating chromium.*

The reaction between potassium chromate and a mercurous salt is to produce a precipitate of *basic* mercurous chromate, which on *boiling* forms the *normal* chromate. (What peculiarity do you notice about this?)

$$3K_2CrO_4 + 4Hg_2(NO_3)_2 + H_2O = 6KNO_3 + 2HNO_3 + \underset{\text{(brown)}}{4Hg_2O,3CrO_3}$$

On boiling,

$$Hg_8Cr_3O_{13} + 2HNO_3 \rightarrow Hg_2(NO_3)_2 + H_2O + \underset{\text{(red)}}{3Hg_2CrO_4}$$

If the mercurous salt is added in slight excess, the precipitation of the chromic acid will be complete, providing that the solution is not too strongly acid. On ignition of the precipitate

$$2Hg_2CrO_4 = Cr_2O_3 + 4Hg + 5O$$

To identify the precipitate as mercurous chromate, try the action of caustic soda.

This method of estimating chromates is an excellent one in every way.

Problem 4.—*Action of water on salts of mercury.*

Both oxides of mercury, HgO and Hg_2O, are weak bases, and nearly all soluble salts of both bases are hydrolysed in

solution in water, forming more or less basic salts according to temperature and dilution. Mercuric chloride and cyanide, however, do not, probably because they are not ionised to any extent in aqueous solution. (See Problem 2.)

BARIUM (p. 41).

Problem 1.—*The equivalent of barium.*

Neutralise a quantity of dilute hot hydrochloric acid with the powdered minerals and filter from excess. The iron is got rid of by first oxidising to ferric chloride (probably by *chlorine* water, as this will avoid evaporating dry to get rid of nitric acid). Avoid a great excess of the oxidising agents and precipitate the iron by adding some barium carbonate [precipitated from a portion of the solution by ammonium carbonate]. See under Iron, Problem 8. Recrystallise the first crop of crystals at least once. Dry by wrapping in filter-paper and putting under pressure, and finally spread out in the air, covered with a large funnel to keep off dust. Dehydrate several grams, and determine the chlorine in about 1·5 grams of the anhydrous substance as silver chloride. [See any book on Elementary Quantitative Analysis.] Calculate the equivalent of barium from your results.

Problem 2.—*The precipitation of barium chromate.*

See Problem 9 under Chromium. The action is similar in every respect to the precipitation of lead chromate under similar conditions.

STRONTIUM (p. 41).

Problem 1.—*The equivalent of strontium.*

Neutralise some hot dilute nitric acid in a porcelain basin with the powdered mineral. Any ferrous carbonate thus forms ferric nitrate Get rid of the iron by adding more

strontianite—exactly as you did with barium. (See Problem 1 under Barium.) Crystallise the filtrate. Any calcium nitrate that may be present will crystallise with it. Now heat the crystallised mass very cautiously till all moisture is expelled, but be careful that decomposition into oxides does not set in. Anhydrous calcium nitrate is soluble in absolute alcohol, whereas strontium nitrate is not. Hence wash the dried mass with successive small quantities of absolute alcohol, till the washings cease to give a test for calcium (dilute sulphuric acid). Then dry the residue again, mix a small portion with 1½ times its weight of pure ammonium chloride, and ignite gently till ammonium chloride vapours cease to come off. Pure strontium chloride, $SrCl_2$, is left, which may be weighed, dissolved in distilled water, and the chlorine precipitated as silver chloride, for the equivalent. The remainder of the dry nitrate is dissolved in water, filtered if necessary, and crystallised, for a specimen of the nitrate.

Problem 2.—On the separation of strontium and calcium.

It will be found by experiment that strontium is *completely* precipitated from solutions of its salts, even in the presence of hydrochloric acid, by both dilute sulphuric acid and ammonium sulphate. The precipitation, however, is *slow*, and requires about five to ten minutes, at blood heat, to be quite complete. It will be found that ammonia plus ammonium oxalate give *no* indication of strontium in the filtrate, if the above conditions are fulfilled.

Calcium is precipitated as $CaSO_4$ both by dilute sulphuric acid and by ammonium sulphate, unless the solution is very dilute. In the presence of excess of dilute hydrochloric acid, however, calcium is *not precipitated at all by ammonium sulphate.* Hence to separate strontium from calcium, add to the solution of the mixed salts not less than its own

volume (or twice its volume if the solution is strong) of 4N hydrochloric acid (bench strength). Ammonium sulphate is then added, and the solution warmed to about 36°C., and stood aside for ten minutes. It is then filtered from the strontium sulphate, which will be completely precipitated. All the calcium will be found in the filtrate.*

CALCIUM (p. 42).

Problem 1.—*The equivalent of calcium.*

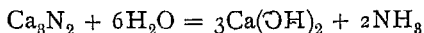
To estimate the purity of the calcium, we may dissolve a clean weighed piece of the metal (·5 gram will be sufficient) in half and half nitric or hydrochloric acid (warm), render alkaline with ammonia, and then acid with acetic acid. Now precipitate the calcium as the oxalate CaC_2O_4, exactly as described under "Estimations with $\frac{N}{10}$ permanganate" [Problem 6, p. 236], and titrate the oxalic acid, and hence the calcium as described. Calculate the percentage of calcium in the specimen. If it is over 99 per cent., the specimen will give a reasonable result for the equivalent.

The equivalent may be found either by the hydrogen displaced from dilute hydrochloric acid, or by synthesising and weighing the oxide, *via* the nitrate.

Problem 2.—*Burning of calcium in air.*

The filtrate will contain the hydroxide $Ca(OH)_2$, as is shown by passing carbon dioxide through it.

The residue will smell of ammonia, showing that calcium nitride is formed, as well as calcium oxide, when the metal burns in air.

$$Ca_3N_2 + 6H_2O = 3Ca(OH)_2 + 2NH_3$$

* The author finds this separation to work extremely well after the separation of barium by potassium chromate in Group IV of the Qualitative Analysis tables.

Problem 3.—*The relative solubilities of several salts of barium, strontium and calcium.*

Commence with normal solutions of the chloride of each metal. Dilute, with water and a little of the required reagent, to known strengths (half normal, tenth normal, $\frac{N}{100}$, $\frac{N}{1000}$, etc.).

Find the limit of dilution at which the precipitate is visible. Hence roughly calculate the solubility of the precipitate.

E.g. To find the limit of the solubility of calcium sulphate, start with N calcium chloride solution and dilute to $\frac{N}{2}$ with water plus a little sodium sulphate solution. If a precipitate falls, on standing for a short time, take 1 c.c. of the $\frac{N}{2}$ solution and dilute to $\frac{N}{4}$, partly with water and partly with the above reagent. Proceed until the precipitate no longer forms.

As reagents use for (*a*) sodium sulphate solution; (*b*) potassium chromate solution: (*c*) *ammonium* carbonate; (*d*) ammonium oxalate.

It will be noticed that the solubility of the strontium salt is always somewhere between the solubilities of the barium and calcium salts. Of the two latter, sometimes the barium, and sometimes the calcium salt, is the more soluble.

BORON (p. 43).

Problem 1.—*The equivalent of boron.*

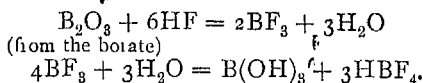
Sufficient details are given with the problem.

Problem 2.—*Action of hydrofluoric acid on boric acid.*

Boron fluoride is produced, which acts on water (like

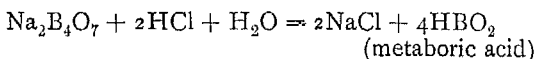
silicon fluoride) to produce boric acid and fluoboric acid, thus—

$$\underset{\text{(from the borate)}}{B_2O_3} + 6HF = 2BF_3 + 3H_2O$$

$$4BF_3 + 3H_2O = B(OH)_3 + 3HBF_4.$$

—Some of the boric acid is precipitated, whilst the fluoboric acid remains in solution. Its potassium salt may be prepared and examined under the action of heat, which decomposes it into $BF_3 + KF$.

Problem 3.—*Preparation of boric acid.*

To a hot strong solution of borax add excess of hydrochloric acid and allow to cool.

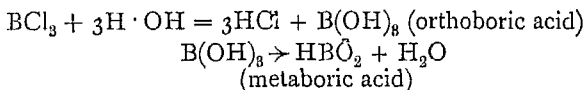
$$Na_2B_4O_7 + 2HCl + H_2O = 2NaCl + \underset{\text{(metaboric acid)}}{4HBO_2}$$

Filter off the crystals on the pump and heat on a water-bath to free from HCl. Recrystallise the boric acid from the minimum quantity of boiling water, to free from sodium chloride.

Problem 4.—*Preparation of boron trichloride.*

Boron trichloride (BCl_3) is formed. Although carbon alone will *not* reduce the oxide (B_2O_3), yet chlorine and carbon between them will effect the reduction.

Boron trichloride and water react like other non-metallic chlorides.

$$BCl_3 + 3H \cdot OH = 3HCl + B(OH)_3 \text{ (orthoboric acid)}$$

$$B(OH)_3 \rightarrow \underset{\text{(metaboric acid)}}{HBO_2} + H_2O$$

ALUMINIUM (p. 44).

Problem 1.—*The equivalent of aluminium.*

Sufficient details are given with the problem.

Problem 2.—Separation of alumina from silica.

The separation of the alumina from the silica is best accomplished by evaporating the finely ground substance with hydrofluoric acid solution and sulphuric acid from a platinum basin. The silica goes off as SiF_4, and from the residue [$Al_2(SO_4)_3$] the alumina may be precipitated by solution in water and adding ammonium chloride and ammonia. Filter, wash, dry and ignite strongly.

Otherwise, fuse with several times its weight of fusion mixture.

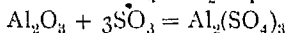
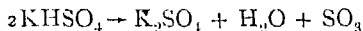
The alumina forms sodium aluminate, and the silica forms sodium silicate, both soluble in water. Dissolve the melt in hot water, *cautiously* add excess of strong hydrochloric acid, evaporate dry on the water-bath, moisten with strong hydrochloric acid, and dry again at 120° C. This renders the silica insoluble, and the aluminium chloride is completely soluble in water. The alumina is precipitated from this solution by ammonia as above.

To get ammonia alum, neutralise one volume of dilute sulphuric acid with ammonia, and three volumes of the same acid with the aluminium hydroxide prepared as above. Mix the filtered solutions and crystallise.

Problem 3.—Alum from bauxite.

If the bauxite is pure (white, containing no iron oxide, Fe_2O_3) it may be fused with potassium bisulphate, $KHSO_4$.

$$2KHSO_4 \rightarrow K_2SO_4 + H_2O + SO_3$$

$$Al_2O_3 + 3SO_3 = Al_2(SO_4)_3$$

Hence to obtain alum, fuse the bauxite with potassium bisulphate, extract the melt with water, and crystallise. Note that the amount of bisulphate required for the solution of the alumina will give us too much potassium sulphate for the alum.

The latter, however, will crystallise out first, and must be recrystallised several times.*

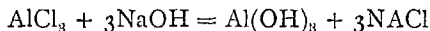
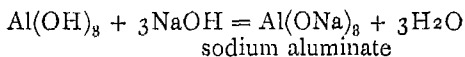
If the bauxite contains iron oxide (red) the alumina must be separated as in Problem 2 by fusion with fusion mixture. The ferric oxide will be unacted on, and the melt is extracted with water and filtered from the unchanged ferric oxide. The solution of sodium aluminate is then acidified with hydrochloric acid and made alkaline with ammonia, and the alum required is prepared from the precipitated hydrate $Al(OH)_3$ as in Problem 2.

Problem 4.—Action of soda on aluminium salts.

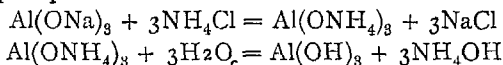
The action is as follows—

$$AlCl_3 + 3NaOH = Al(OH)_3 + 3NACl$$

Soluble in excess of soda thus—

$$Al(OH)_3 + 3NaOH = Al(ONa)_3 + 3H_2O$$
sodium aluminate

On boiling, this reaction is *not* reversed very appreciably. Hence separation of aluminium from chromium in Group III. A in Qualitative Analysis.

When sodium aluminate is boiled with ammonium chloride, ordinary double decomposition takes place, and ammonium aluminate is formed. This, however, suffers immediate and complete hydrolysis, the hydroxide $Al(OH)_3$ being precipitated.

$$Al(ONa)_3 + 3NH_4Cl = Al(ONH_4)_3 + 3NaCl$$
$$Al(ONH_4)_3 + 3H_2O = Al(OH)_3 + 3NH_4OH$$

Problem 5.

The substance was cryolite, Na_3AlF_6. Explain fully how you set about its analysis.

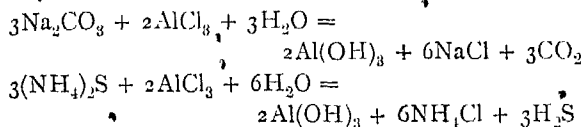
Problem 6.—The carbonate and sulphide of aluminium.

Neither carbonate nor sulphide of aluminium are formed,

* If crystallised at 100°C. the K_2SO_4 will crystallise out first. The separation is far more complete at this temperature.

each salt suffering complete hydrolysis, the result being that the hydroxide is formed, thus—

$$3Na_2CO_3 + 2AlCl_3 + 3H_2O = 2Al(OH)_3 + 6NaCl + 3CO_2$$

$$3(NH_4)_2S + 2AlCl_3 + 6H_2O = 2Al(OH)_3 + 6NH_4Cl + 3H_2S$$

CARBON (p. 45).

Problem 1.—*The equivalent of carbon.*

The apparatus is simply a hard-glass tube of sufficient length to contain a porcelain boat with the carbon, and

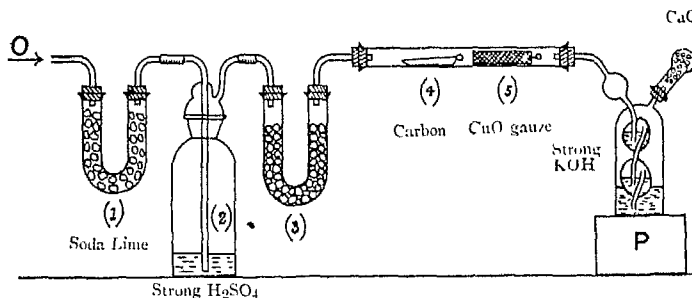



FIG. 14.

about six inches of pure copper oxide (oxidised copper gauze). The latter is heated *before* the carbon is burnt, and any carbon monoxide formed will be oxidised to dioxide. The oxygen is supplied from a gas-holder, and should have been made from potassium chlorate *alone* (NOT chlorate plus manganese dioxide, as the oxygen from these contains traces of chlorine). It should be passed over soda-lime to absorb any carbon dioxide, and then dried. The dioxide formed by the burning carbon is absorbed in a potash-bulb similar to that used in organic combustions.

Problem 2.—*Estimation of carbon dioxide in a carbonate.*

Fresenius' apparatus is as good as any, and possesses the advantage of great simplicity. In careful hands it yields excellent results.

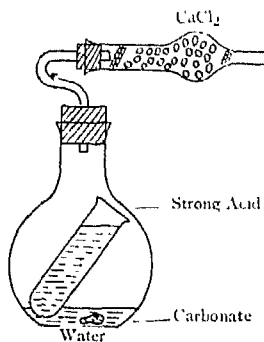
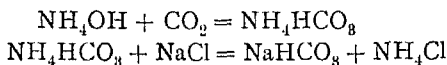



FIG. 15.

Weigh the whole apparatus containing some water in the flask and some strong HCl in the tube. Introduce the carbonate and weigh again. Tip the acid out of the tube, and when the action is complete, put on a wire gauze and heat with a very small flame till it *just begins* to boil. Allow to cool and weigh again.

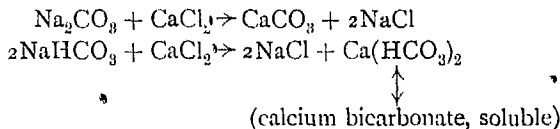
Problem 3.—*The ammonia-soda process.*

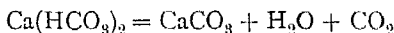
A precipitate settles out which may be proved to be sodium bicarbonate, $NaHCO_3$. The action is—

$$NH_4OH + CO_2 = NH_4HCO_3$$
$$NH_4HCO_3 + NaCl = NaHCO_3 + NH_4Cl$$

This is the **Solvay** process for the manufacture of sodium carbonate. On heating the bicarbonate it evolves water and carbon dioxide, which can be used again. The carbon dioxide is originally supplied from heated limestone, and the quicklime which results can be used to turn out ammonia from the residual ammonium chloride. Thus the process is more or less of a cycle, and is therefore remarkably economical. The only drawback is the initial cost of the plant.

Problem 4.—*The carbonates of calcium.*

The reactions are as follows—

$$Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 + 2NaCl$$
$$2NaHCO_3 + CaCl_2 \rightarrow 2NaCl + Ca(HCO_3)_2$$
$$\updownarrow$$
(calcium bicarbonate, soluble)

On boiling the latter solution, the reverse action takes place.

$$Ca(HCO_3)_2 = CaCO_3 + H_2O + CO_2$$

and the normal carbonate is therefore precipitated. Compare magnesium carbonates and bicarbonate, also iron carbonate and bicarbonate.

Note that *unlike* magnesium, there is *no basic carbonate* of calcium. Lime is a much stronger base than magnesia.

ORGANIC PROBLEMS (p. 46).

Problem 1.—*Formula of a gaseous hydrocarbon.*

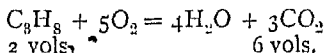
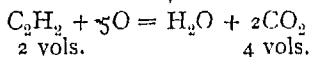
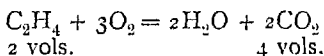
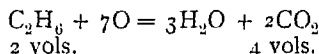
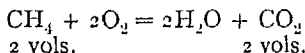
A few equations are given below—

$$\underset{2\ \text{vols.}}{CH_4} + 2O_2 = 2H_2O + \underset{2\ \text{vols.}}{CO_2}$$

$$\underset{2\ \text{vols.}}{C_2H_6} + 7O = 3H_2O + \underset{4\ \text{vols.}}{2CO_2}$$

$$\underset{2\ \text{vols.}}{C_2H_4} + 3O_2 = 2H_2O + \underset{4\ \text{vols.}}{2CO_2}$$

$$\underset{2\ \text{vols.}}{C_2H_2} + 5O = H_2O + \underset{4\ \text{vols.}}{2CO_2}$$

$$\underset{2\ \text{vols.}}{C_3H_8} + 5O_2 = 4H_2O + \underset{6\ \text{vols.}}{3CO_2}$$

In all the above combustions, note that the volume of carbon dioxide formed = x times the volume of the hydro-

carbon, where x is the number of carbon atoms in the hydrocarbon. This, of course, follows from the simple fact that the carbon dioxide molecule only contains one atom of carbon. Hence the ratio of the volume of carbon dioxide formed to the original volume of the hydrocarbon tells us at once how many carbon atoms there are in the hydrocarbon molecule.

Further, carbon dioxide contains its own volume of oxygen, also the excess of oxygen left after the combustion is measured directly, and hence the volume of oxygen that has gone to form water is known. Twice this volume is the volume of hydrogen in that water. Hence the volume of hydrogen in the hydrocarbon molecule is known, and hence, by Avogadro's law, the number of molecules of hydrogen in the hydrocarbon molecule.

Example.—10 c.c. of a hydrocarbon are exploded with 40 c.c. of oxygen. After explosion the volume is 30 c.c. After absorption of carbon dioxide it is 20 c.c. Find the formula of the gas.

The volume of carbon dioxide = 30 − 20 = 10 c.c.
= volume of hydrocarbon.

∴ *the hydrocarbon molecule contains* 1 *atom of carbon.*

Also—

10 c.c. of carbon dioxide contain 10 c.c. of oxygen.

20 c.c. of oxygen are left, *i. e.* 30 c.c. are accounted for.

∴ 40 − 30 = 10 c.c. of oxygen have gone to form water and have required 20 c.c. of hydrogen.

i. e. 10 c.c. of the gas contain 20 c.c. of hydrogen.

∴ 1 volume " " 2 volumes "
∴ 1 molecule " " 2 molecules "
∴ 1 " " " 4 atoms "

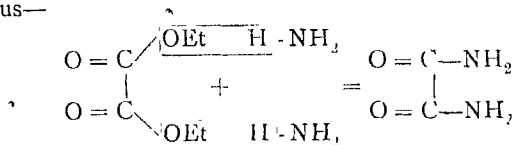
i. e. *the formula is* CH_4.

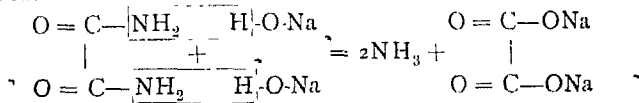
Problem 2.—Action of ammonia on ethyl oxalate.

When hydrolysed by caustic soda, ammonia is evolved, and on evaporating the residue, and treating some with hot strong sulphuric acid, both carbon monoxide and dioxide are given off, showing the presence of an oxalate, which can be confirmed by acidifying a further portion of the residue with acetic acid and to this solution adding calcium chloride. Calcium oxalate is precipitated, which when dissolved in dilute sulphuric acid, decolorises permanganate in the manner characteristic of oxalic acid.

The evolution of ammonia suggests either an ammonium salt or an amide. The empirical formula is against an ammonium salt, and in favour of an amide (*two* NH_2 groups).

The well-known action of ammonia on *other* esters confirms this. The product of hydrolysis being sodium oxalate, we thus conclude that the substance is oxamide, the double amide of oxalic acid, and that it is formed thus—

$$\begin{array}{l} O=C\diagup OEt \quad H\text{-}NH_2 \\ \quad | \qquad\quad + \\ O=C\diagdown OEt \quad H\text{-}NH_2 \end{array} = \begin{array}{l} O=C\text{—}NH_2 \\ \quad | \\ O=C\text{—}NH_2 \end{array}$$

The hydrolysis by caustic soda will then take place, thus—

$$\begin{array}{l} O=C\text{—}NH_2 \quad H\text{-}O\text{-}Na \\ \quad | \qquad\quad + \\ O=C\text{—}NH_2 \quad H\text{-}O\text{-}Na \end{array} = 2NH_3 + \begin{array}{l} O=C\text{—}ONa \\ \quad | \\ O=C\text{—}ONa \end{array}$$

Problem 3.—Action of alcoholic ammonia on ethyl oxalate

The products of distillation will be a watery liquid smelling strongly of ammonia. If the ammonia be neutralised by hydrochloric acid, an ethereal smell also will be

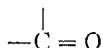
noticed. Redistil, and collect the first portion that comes over. What does it smell like? Does it not remind you of alcohol? Apply the iodoform test for alcohol. It is found to be present

Returning to the residue in the flask from the original distillation, on neutralising with dilute sulphuric acid, evaporating dry, and treating some of the residue with strong sulphuric acid, we get evidence of an oxalate, carbon monoxide and dioxide being evolved. Confirm this by dissolving the rest in acetic acid and adding calcium chloride. Calcium oxalate is precipitated.

Thus the products of hydrolysis are—

Oxalic acid, ammonia, and ethyl alcohol.

This suggests the presence in the compound of—

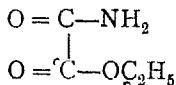
(*a*) an oxalic acid residue
$$\begin{array}{l}—C = O \\ \quad | \\ —C = O\end{array}$$

(*b*) Either an ammonium salt or an amide.

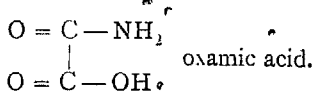
(*c*) An ethoxyl group (as in an ethyl ester) $—O—C_2H_5$.

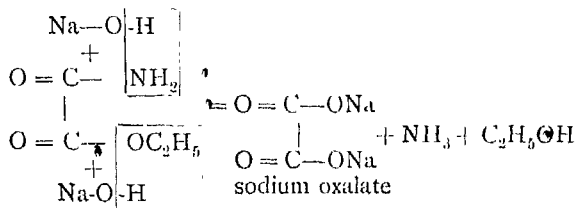
This shows us that the substance is either ethyl ammonium oxalate, or the ethyl ester of the monamide of oxalic acid.

If the first, there would be nine hydrogen atoms in the molecule; if the latter, only seven.

You are told that there *are* seven. Hence the substance is—

$$\begin{array}{l}O = C—NH_2 \\ \qquad | \\ O = C—OC_2H_5\end{array}$$

i.e. it is half oxalic ester and half oxamide. It is known as ethyl oxamate or oxamethane, the free (unknown) acid being

$$\begin{array}{l}O = C—NH_2 \\ \qquad | \\ O = C—OH\end{array} \quad \text{oxamic acid.}$$

The hydrolysis then will proceed thus—

$$\begin{array}{l} Na—O\text{-}H \\ \quad + \\ O = C— \quad NH_2 \\ \quad | \\ O = C— \quad OC_2H_5 \\ \quad + \\ Na\text{-}O\text{-}H \end{array} = \begin{array}{l} O = C—ONa \\ \quad | \\ O = C—ONa \\ \text{sodium oxalate} \end{array} + NH_3 + C_2H_5OH$$

Problem 4.—*Constitutional formula of* C_8H_9NO.

(i) After heating with strong hydrochloric acid, cooling, and making alkaline, we notice an oily liquid is formed, that has the characteristic odour of aniline. Collect these few drops carefully, and apply the bleaching-powder test for aniline. It *is* aniline.

(ii) The distillate possesses the characteristic smell of acetic acid, whose presence can be shown by—

(*a*) The amyl acetate test.

(*b*) The ferric acetate test.

In the residue will be found aniline sulphate, for on making alkaline with caustic soda, aniline is obtained.

(iii) With concentrated caustic soda the distillate will contain aniline, and the residue, after evaporating dry, will give, after suitable treatment, the tests for an acetate.

At first sight, then, the substance would seem to be aniline acetate. This, however, requires the formula $C_8H_{11}NO_2$. Note that the formula given is this $-H_2O$. Hydrolysis evidently supplies this H_2O, giving aniline and acetic acid. Hence the substance contains—

(*a*) An aniline residue, C_6H_5NH—

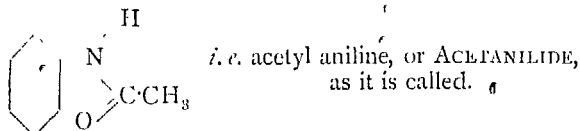
(*b*) An acetyl group, CH_3CO—

If these groups are joined together by the free valency on each, we get a substance which would behave as this

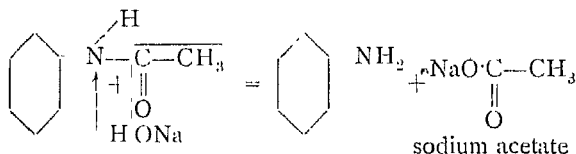
substance has done, and which would have the required formula C_8H_9NO.

Hence the substance must be—

$$C_6H_5-N(H)-C(=O)-CH_3$$

i. e. acetyl aniline, or ACETANILIDE, as it is called.

The hydrolysis will proceed thus—

$$C_6H_5-N(H)-C(=O)-CH_3 + HONa = C_6H_5NH_2 + NaO{\cdot}C(=O)-CH_3$$

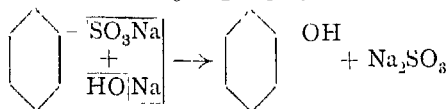
sodium acetate

Problem 5.—Action of fused soda on a sulphonate.

On rendering the fused mass acid with hydrochloric acid we shall smell—

(*a*) Sulphur dioxide, showing the presence of a sulphite.

(*b*) Phenol.

The action of fused caustic soda on the sulphonate has been to replace the —SO_3Na group by —OH, thus—

$$C_6H_5-SO_3Na + HONa \rightarrow C_6H_5OH + Na_2SO_3$$

The phenol, of course, will form non-volatile sodium phenate, C_6H_5ONa, with some more NaOH, and acidification sets the phenol free. This is a general method of replacing a hydrogen atom in the benzene ring by hydroxyl, by first sulphonating, and then fusing the purified sulphonate with an alkali. The phenol formed will be recovered either by steam distillation or ether extraction, according to circumstances.

Problem 6.—*Reaction between ammonia and carbon dioxide in absence of water.*

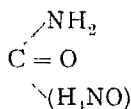
The dried crystals will smell of ammonia. Hence we deduce the ammonium salt of a weak acid.

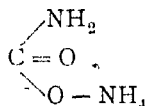
Calcium chloride solution and this solution *may* give us a precipitate of calcium carbonate. On filtering and boiling this filtrate, a further and larger precipitate of calcium carbonate is obtained.

This suggests either (1) a bicarbonate; (2) something that produces a carbonate on hydrolysis.

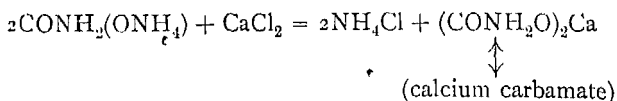
With nitrous acid the substance will be found to evolve nitrogen, *i.e.* it is either an acid amide or a primary amine. With sodium hypobromite it evolves nitrogen, and sodium carbonate will be left, confirming the fact that it is an amide of carbonic acid. Its formula shows that it cannot be urea, therefore the only alternative is that it is a derivative of urea, and that one of the NH_2 groups is still intact.

Hence we can write—

$$C{=}O \begin{cases} NH_2 \\ (H_4NO) \end{cases}$$

The (NH_4) has been shown to be present as an ammonium salt, hence we are reduced to writing it.

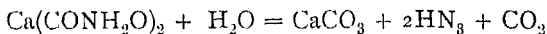
$$C{=}O \begin{cases} NH_2 \\ O - NH_4 \end{cases}$$

i.e. the substance is half way between ammonium carbonate and urea. The free (unknown) acid is called *carbamic acid*, from its constitution. Hence the substance is *ammonium carbamate*, and the above reactions may be formulated thus:—

With calcium chloride—

$$2CONH_2(ONH_4) + CaCl_2 = 2NH_4Cl + (CONH_2O)_2Ca$$

(calcium carbamate)

Calcium carbamate is soluble in water, hence if the substance is free from carbonate, calcium chloride will produce no precipitate.

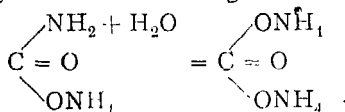
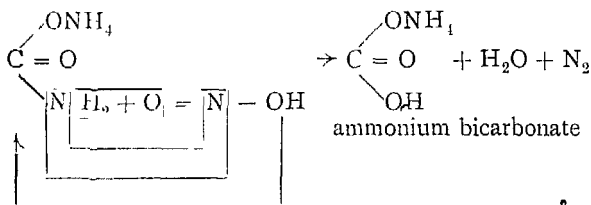
On boiling,

$$Ca(CONH_2O)_2 + H_2O = CaCO_3 + 2HN_3 + CO_2$$

The hydrolysis of the carbamate goes thus—

$$C{=}O\begin{cases}NH_2 + H_2O\\ ONH_4\end{cases} = C{=}O\begin{cases}ONH_4\\ ONH_4\end{cases}$$

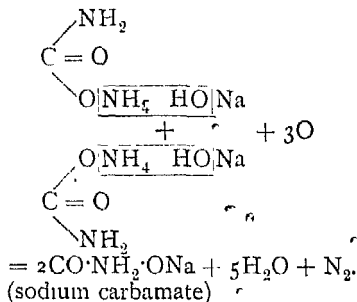
with nitrous acid—

$$C{=}O\begin{cases}ONH_4\\ N\,H_2 + O = N - OH\end{cases} \rightarrow C{=}O\begin{cases}ONH_4\\ OH\end{cases} + H_2O + N_2$$

ammonium bicarbonate

and with sodium hypochlorite or hypobromite—

$$\begin{matrix}C{=}O\begin{cases}NH_2\\ O\,NH_4\;\;HO\,Na\end{cases}\\ + \\ C{=}O\begin{cases}O\,NH_4\;\;HO\,Na\\ NH_2\end{cases}\end{matrix} + 3O$$

$$= 2CO{\cdot}NH_2{\cdot}ONa + 5H_2O + N_2.$$

(sodium carbamate)

Problem 7.—Separation of benzene and benzolene.

The only thing to be done is to convert one of them into a derivative which is either solid or has a much higher boiling point.

This may be done, for instance, by treating with concentrated nitric and sulphuric acids, when nitrobenzene will be produced, but no nitric paraffin. Fractionation can now be accomplished with ease, as nitrobenzene has a high boiling point. The benzene is recovered from the nitrobenzene by conversion into aniline, diazotising, and boiling the diazo salt with 50 per cent. alcohol in the usual way. (See any Organic Chemistry text-book.)

Problem 8.—Molecular weight of an organic acid.

Neutralise the acid with dilute ammonia, and boil off any excess of ammonia. Cool, add silver nitrate solution, and stand for a few minutes. [*N.B.*—If no precipitate falls, the silver salt is moderately soluble in water, and stronger solutions must be used.] Filter off the precipitate on the pump, and wash with a considerable number of *small* portions of distilled water. This is best done by artificial light. Dry in the dark in the steam oven. Heat a weighed portion in a porcelain crucible with the lid on, *cautiously at first*, and afterwards strongly with lid off. Weigh the residual silver. If the acid is monobasic, calculate what weight of the silver salt contains 108 grams (1 atom) of silver. If the acid is n basic, calculate the weight that contains $n \times 108$ grams of silver. This will be the molecular weight of the silver salt. From this, subtract $n \times 108$, and add $n \times 1$ (*i.e.* substitute hydrogen for silver), and the result will obviously be the molecular weight of the acid.

Problem 9.—*Distinction between primary, secondary and tertiary amines.*

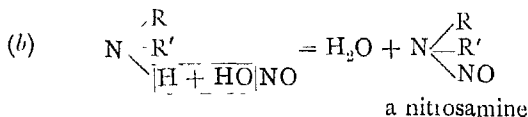
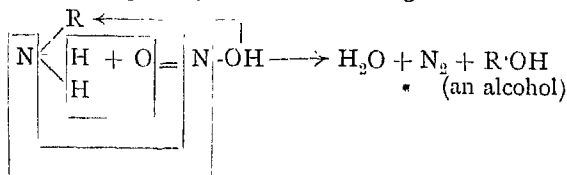
We have obviously to decide between a primary, secondary or a tertiary amine. This is easily accomplished by treatment with nitrous acid. Treat the amine with sodium nitrite solution, followed by dilute sulphuric acid. This reacts as follows:—

(*a*) With a primary amine, on warming—

$$N \begin{cases} R \\ H \\ H \end{cases} + O = N\text{-}OH \longrightarrow H_2O + N_2 + R\cdot OH$$

(an alcohol)

(*b*)

$$N \begin{cases} R \\ R' \\ H \end{cases} + HO|NO = H_2O + N \begin{cases} R \\ R' \\ NO \end{cases}$$

a nitrosamine

The nitrosamines are insoluble oily liquids. Separate any oily drops which may form, and apply LIEBERMANN'S reaction for a nitroso-compound. (Add to it some strong sulphuric acid and some phenol. A brown coloration is obtained, turning green and finally dark blue.)

(*c*) Tertiary amines do not react with HNO_2.

Confirm your deductions quantitatively by preparing the quaternary ammonium salt by treatment with methyl iodide, and finding its molecular weight by the chlorplatinate method.

Problem 10.—*Distinction between primary, secondary and tertiary alcohols.*

There are two ways of deciding between primary secondary and tertiary alcohols.

1. Oxidise with chromic acid, and distil.

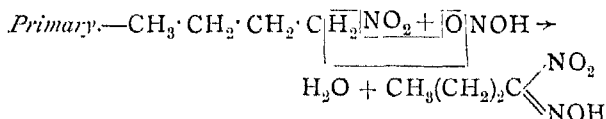
(*a*) A primary alcohol gives only an aldehyde, recognised by its special reactions.

(*b*) A secondary alcohol gives only a ketone, recognised by its special reactions.

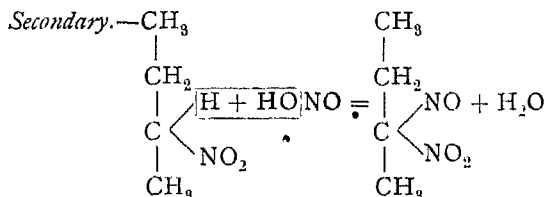
(*c*) A tertiary alcohol gives a variety of oxidation products, generally at least one acid and a ketone, and each contains less carbon than the original alcohol.

2. By a method due to Victor Meyer. If the alcohol be converted to the corresponding nitroparaffin, we shall get a primary, secondary or tertiary nitroparaffin according as the alcohol is primary, secondary or tertiary. The nitroparaffins can be distinguished by the action of nitrous acid on them, thus:—

Primary.—$CH_3 \cdot CH_2 \cdot CH_2 \cdot C\,\boxed{H_2}\,NO_2 + \boxed{O}\,NOH \rightarrow$

$$H_2O + CH_3(CH_2)_2C\begin{cases} NO_2 \\ NOH \end{cases}$$

The product is known as a *nitrolic acid* (in this case butyl nitrolic acid), or an isonitroso-nitroparaffin. They are colourless, but solutions of their potassium salts are bright red.

Secondary.—

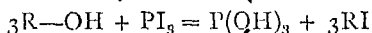
$$\begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ C \begin{cases} H + HO\,NO \\ NO_2 \end{cases} \\ | \\ CH_3 \end{array} = \begin{array}{l} CH_3 \\ | \\ CH_2 \\ | \\ C \begin{cases} NO \\ NO_2 \end{cases} \\ | \\ CH_3 \end{array} + H_2O$$

This is a *nitroso*-nitroparaffin, and like all nitroso bodies, its solution is blue or green.

Tertiary.—Obviously cannot act with nitrous acid.

Hence the test is applied thus—

The alcohol is treated carefully with PI_3 (phosphorus and iodine in the right proportions) and distilled.

This gives us the alkyl iodide—

$$3R—OH + PI_3 = P(OH)_3 + 3RI$$

The iodide is dried and distilled from dry silver nitrite. This gives us a mixture of the nitrite and the nitroparaffin, $R—NO_2$ and RO—N : O.

The distillate is put into a test-tube and some *sodium* nitrite solution is added, followed by a few drops of dilute sulphuric acid.

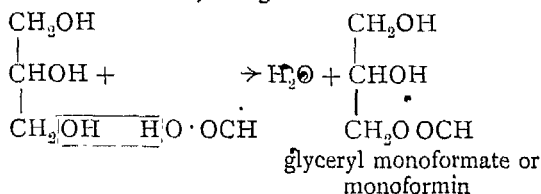
If the solution becomes blue or green, a nitroso compound has been formed. The nitroparaffin, and therefore the alcohol, must be *secondary*.

If the solution remains colourless, either a nitrolic acid has been formed, or nothing. Add potash till alkaline, when a red colour proves the presence of a nitrolic acid, *i.e.* the alcohol was *primary*, or if still colourless, that nitrous acid has had no action, i. e. *tertiary*.

Problem 11.—*Action of oxalic acid on glycerine.*

Glycerine and oxalic acid, when heated together, rapidly evole carbon dioxide.

Hence COOH | COOH has probably formed CO_2 and H · COOH (formic acid). The formic acid will react with the glycerine in the usual manner that an acid and an alcohol react, and give—

glyceryl monoformate or monoformin

This will be hydrolysed by the water of crystallisation in the oxalic acid, and we shall get glycerine and formic acid (the *reverse* of the above reaction). The acid will distil, and may be identified in the usual way. More may be recovered from the residue in the retort by steam distillation.

Lead formate should be prepared from the acid by adding a slight excess of lead carbonate to the hot, rather dilute acid, filtering, and allowing to crystallise slowly. A further crop can be obtained from the mother liquor.

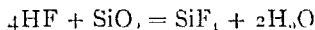
SILICON (p. 50).

Problem 1.—*The equivalent of silicon.*

Sufficient details have been given with the problem.

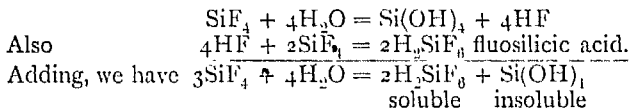
Problem 2.—*Action of hydrofluoric acid on silica.*

The action of hydrofluoric acid on silica is—

$$4HF + SiO_2 = SiF_4 + 2H_2O$$

The reverse action also takes place; the way it goes is determined by the relative amounts of hydrofluoric acid or of water present. If the acid be generated in the presence of the silica by the action of strong sulphuric acid on calcium fluoride, the above reaction goes almost completely from left to right. On passing the silicon tetrafluoride into water, gelatinous orthosilicic acid is produced.

$$SiF_4 + 4H_2O = Si(OH)_4 + 4HF$$

Also $\quad 4HF + 2SiF_4 = 2H_2SiF_6$ fluosilicic acid.

Adding, we have $\quad 3SiF_4 + 4H_2O = 2H_2SiF_6 + Si(OH)_4$

soluble insoluble

On filtering off the gelatinous silicic acid, and washing, drying and igniting it, we have pure silica left. The filtrate may be neutralised with potassium carbonate, and the *sparingly soluble* potassium salt is readily obtained. When heated it gives off SiF_4, leaving 2KF. The barium salt of

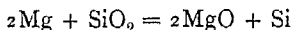
this acid resembles barium sulphate in its insolubility in acids.

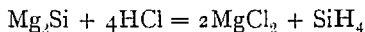
Problem 3.—Pure silica from kaolin.

From the previous example, mix with plenty of calcium fluoride and heat with strong sulphuric acid. Pass the evolved gas (SiF_4) into water, using a funnel as delivery tube, and filter, wash, dry, and ignite the silicic acid. The above method is *the best* for obtaining silica from any silicate. (Compare Problem 2 under Aluminium.)

Problem 4.—Preparation of silicon from silica.

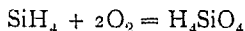
The reactions are—

$$2Mg + SiO_2 = 2MgO + Si$$

A little Mg_2Si may be formed, which is decomposed by acid thus—

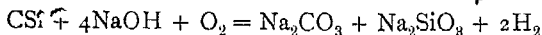
$$Mg_2Si + 4HCl = 2MgCl_2 + SiH_4$$

The SiH_4 so obtained is spontaneously inflammable.

Problem 5.—Preparation of hydrogen silicide.

By the action of acids (dilute) on magnesium silicide (Mg_2Si). The apparatus in which it is generated should have the air displaced by coal-gas, as in the preparation of phosphine. Hydrogen silicide is spontaneously inflammable as thus prepared, and burns to silicic acid.

$$SiH_4 + 2O_2 = H_4SiO_4$$

Problem 6.

The substance supplied was carborundum (CSi). It is acted on neither by heat nor acids, but fused alkalis act on it, producing a mixture of carbonate and silicate. Fuse the finely powdered substance gently with caustic soda and free access of air.

$$CSi + 4NaOH + O_2 = Na_2CO_3 + Na_2SiO_3 + 2H_2$$

The melt is dissolved in water and tested for both carbonate and silicate, by adding dilute hydrochloric acid,

when carbon dioxide is evolved. Ammonium chloride and ammonia will produce gelatinous silicic acid (if the hydrochloric acid does not) as ammonium silicate is completely hydrolysed by water.

Problem 7.—*Actions of chlorine and hydrochloric acid gas on silicon.*

The action of chlorine on heated silicon is to produce silicon tetrachloride ($SiCl_4$), a volatile liquid, B.P. 59° C. It reacts *violently* with water (*cf.* carbon tetrachloride), producing hydrochloric acid and orthosilicic acid, and hence is a true acid chloride.

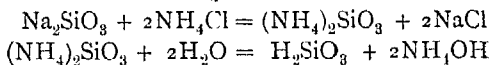
$$SiCl_4 + 4H \cdot OH = Si(OH)_4 + 4HCl$$

The action of hydrochloric acid gas is to produce a mixture of silicon tetrachloride and silico-chloroform, $SiHCl_3$, B.P. 34° C. Separation by careful fractionation, with exclusion of moisture.

Silico-chloroform reacts with water producing hydrochloric acid and silicoformic anhydride ($H \cdot Si \cdot O \cdot O \cdot O \cdot Si \cdot H$), a white voluminous mass, soluble in alkalis to produce silicates and hydrogen. (Write graphic equations.)

Problem 8.—*Action of ammonium chloride on a soluble silicate.*

Ammonium silicate is probably first formed but is completely hydrolysed by water, producing ammonia and silicic acid, thus—

$$Na_2SiO_3 + 2NH_4Cl = (NH_4)_2SiO_3 + 2NaCl$$
$$(NH_4)_2SiO_3 + 2H_2O = H_2SiO_3 + 2NH_4OH$$

TIN (p. 53).

Problem 1.—*The equivalents of tin.*

Sufficient details are given with the problem.

Problems 2 and 3.—The chlorides of tin.

Stannous chloride is a fairly powerful reducing agent. It will reduce mercuric chloride to mercurous chloride, and finally to mercury. It reduces ferric salts to ferrous immediately, and strong hot sulphuric acid is reduced to sulphur dioxide. In all these reactions the tin goes to the stannic state, and hence we should expect only powerful reducing agents to reduce stannic chloride to stannous. Tin itself, also nascent hydrogen, will do this.

Problem 4.—A "concentration" tin cell.

The arrangement is one of the so-called "concentration" cells, and a deposit of crystalline tin will form slowly on the lower end of the tin rod. The explanation is briefly this: at the top, in the dilute solution, the tendency of the tin to go into solution is greater than the osmotic pressure of the tin ions. Hence + *ve* ions of tin go off into solution, and the top end of the rod becomes − *ve*. At the bottom, the osmotic pressure of the tin ions is greater than the solution pressure of the tin, and hence + *ve* tin ions deposit themselves, gradually forming crystals. There will thus be a fall of potential along the tin rod from bottom to top, and the solution will tend to become of equal strength both top and bottom. (Explanation due to NERNST.)

LEAD (p. 54).

Problem 1.—The equivalents of lead.

In finding the equivalent of tetravalent lead by the reduction of lead dioxide, it should be reduced, after weighing, to litharge by heating in air. If an attempt be made to reduce lead dioxide in hydrogen, an explosion that will spoil the experiment will certainly result. In any case, use a boat of copper foil, not of porcelain, to contain the oxide.

Problems 2 and 3.—Chemistry of the oxides of lead.

Litharge is distinctly alkaline to litmus, and dissolves completely in acids to form salts and water.

The three higher oxides give off oxygen on heating and leave litharge. They also give off chlorine with hot strong hydrochloric acid, and oxygen with hot strong sulphuric acid, and are therefore to be regarded as peroxides.

The action of nitric acid on the four oxides is similar to its action on the oxides of manganese of similar formula.

PbO dissolves completely to form lead nitrate.

Pb_2O_3 is partly dissolved, forming lead nitrate (test for in the filtrate and obtain lead nitrate crystals), and a brown powder which is obviously PbO_2. (Prove this by drying and heating.)

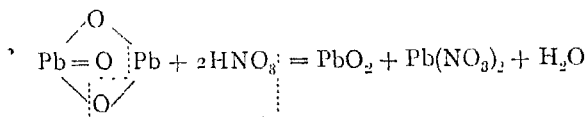
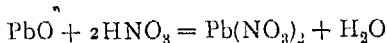
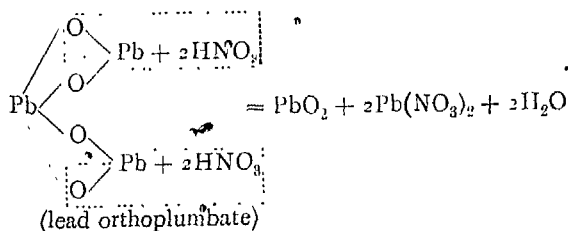
Pb_3O_4 acts similarly, whereas PbO_2 is not affected.

Hence we must regard Pb_2O_3 and Pb_3O_4 as salts of lead with plumbic acid, PbO_2, and the reactions may be formulated thus—

$$PbO + 2HNO_3 = Pb(NO_3)_2 + H_2O$$

$$\mathrm{Pb{=}O}\left<\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right>\mathrm{Pb} + 2HNO_3 = PbO_2 + Pb(NO_3)_2 + H_2O$$

(lead metaplumbate)

$$\mathrm{Pb}\left<\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right>\begin{matrix}\left<\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right>\mathrm{Pb} + 2HNO_3\\ \\ \left<\begin{matrix}\mathrm{O}\\ \mathrm{O}\end{matrix}\right>\mathrm{Pb} + 2HNO_3\end{matrix} = PbO_2 + 2Pb(NO_3)_2 + 2H_2O$$

(lead orthoplumbate)

This could obviously be confirmed quantitatively by finding the ratio of the lead dissolved as nitrate to that left as PbO_2 in each case, an exercise that may be left to the student, with the warning that results can only be expected from absolutely pure oxides.

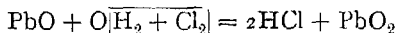
Since lead belongs to the same group as carbon in the periodic classification, the oxides Pb_2O_3 and Pb_3O_4 can be regarded as derived from the acids, metaplumbic $PbO(OH)_2$ and orthoplumbic $Pb(OH)_4$, which correspond to $CO(OH)_2$ [carbonic acid] and $C(OH)_4$ [orthocarbonic acid], derivatives of *both* of which latter acids are well known.

Calcium plumbate, $Pb\begin{matrix} \diagup O \diagdown \\ = O \\ \diagdown O \diagup \end{matrix}Ca$ is also well known.

Problem 4.—*Action of chlorine water on litharge.*

Testing with litmus, we note that an acid is produced, which must be hydrochloric. A brown powder is produced, which is obviously lead dioxide. (Prove by filtering, washing, drying and heating.)

The action therefore must be—

$$PbO + O\boxed{H_2 + Cl_2} = 2HCl + PbO_2$$

The oxygen being *nascent* in the presence of litharge, is enabled to oxidise it to the dioxide as molecular oxygen cannot do.

Problem 5.—*Action of dilute alkali on lead chromate.*

When lead chromate has been boiled with lime-water or dilute caustic soda, it is noticed that the yellow powder turns into a fiery red one, and that on filtering at the end of the action, the filtrate is yellow, and on being acidified with acetic acid answers to the usual tests for a chromate.

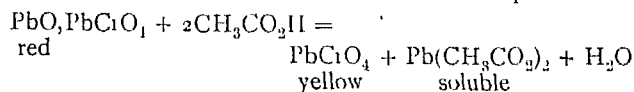
That the red powder is *not red lead* will be immediately

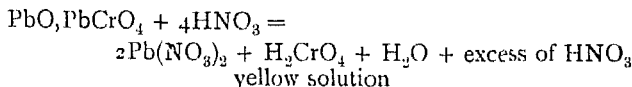
seen by its action with, say, dilute nitric acid.) Its actions with the reagents suggested will be as follows—

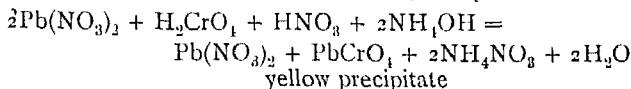
(*a*) Dilute acetic acid. The substance turns yellow again, and looks like the original lead chromate. On filtering, and testing the filtrate for *lead*, we find that plenty of lead has dissolved as lead acetate.

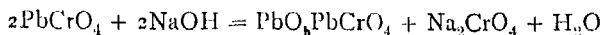
(*b*) The red powder is completely soluble in dilute nitric acid to an orange solution. On just neutralising with ammonia, yellow lead chromate is reprecipitated.

The conclusion from (*a*) is that the red powder is a *basic* chromate, since lead chromate is quite insoluble in acetic acid. Assuming its formula to be, say, $PbO,PbCrO_4$, we see that the action with acetic acid is at once explained.

$$\underset{\text{red}}{PbO,PbCrO_4} + 2CH_3CO_2H = \underset{\text{yellow}}{PbCrO_4} + \underset{\text{soluble}}{Pb(CH_3CO_2)_2} + H_2O$$

Also in (*b*) the action will be—

$$PbO,PbCrO_4 + 4HNO_3 = \underset{\text{yellow solution}}{2Pb(NO_3)_2 + H_2CrO_4} + H_2O + \text{excess of } HNO_3$$

On neutralising this excess of acid by NH_4OH—

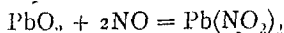
$$2Pb(NO_3)_2 + H_2CrO_4 + HNO_3 + 2NH_4OH = Pb(NO_3)_2 + \underset{\text{yellow precipitate}}{PbCrO_4} + 2NH_4NO_3 + 2H_2O$$

Hence the action with caustic soda may be formulated—

$$2PbCrO_4 + 2NaOH = PbO,PbCrO_4 + Na_2CrO_4 + H_2O$$

A more or less basic chromate will be formed according to the amount of soda used and the time of the action.

Problem 6.—Action of nitric oxide on lead dioxide.

A white powder will be formed, soluble in water, that turns out to be lead nitrite. If boiled with excess of

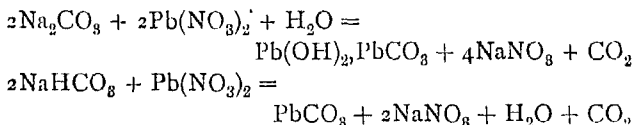
NH_4Cl, to destroy the nitrite ($NH_4NO_2 \rightarrow 2H_2O + N_2$), no nitrate will be found. Hence we may write—

$$PbO_2 + 2NO = Pb(NO_2)_2$$

The action is not complete, however, and overheating will destroy the $Pb(NO_2)_2$, leaving red-lead and, finally, litharge.

Problem 7.—The carbonates of lead.

It will be found that sodium carbonate precipitates a basic carbonate, whilst sodium bicarbonate precipitates the normal carbonate. Carbon dioxide will be given off in *both* cases, hence the reason for saying that sodium carbonate gives a basic carbonate.

$$2Na_2CO_3 + 2Pb(NO_3)_2 + H_2O = Pb(OH)_2,PbCO_3 + 4NaNO_3 + CO_2$$

$$2NaHCO_3 + Pb(NO_3)_2 = PbCO_3 + 2NaNO_3 + H_2O + CO_2$$

If this latter precipitate be washed with carbonic acid solution, then with alcohol, and finally with ether, and dried in the steam oven, the carbon dioxide may be estimated in Fresenius' apparatus, using *nitric* acid, and the percentage should be that required by the formula $PbCO_3$.

Problem 8.—Sensibility of tests for lead.

Make a normal solution of lead acetate, and dilute to any required strength with dilute hydrochloric acid. By repeating this, and noting the last strength at which hydrogen sulphide gives a dark coloration (PbS), it will be found that lead can just be detected in this way in a $\frac{N}{100,000}$ solution, *i.e.* since a N solution of lead contains 103·5 grams of lead per litre, about 1 part of lead in 1,000,000 can be detected in this way.

If we dilute with caustic soda instead of with hydrochloric acid, we shall find the reaction to be about twice as delicate, a perceptible coloration being produced by H_2S in about a $\frac{N}{200,000}$ solution, which contains 1 part of lead in 2,000,000 of solution.

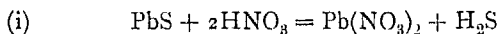
Hence, to test for small quantities of hydrogen sulphide, always use an *alkaline* lead solution.

Problem 9.—Properties of lead sulphate (preliminary to Problem 10).

Lead sulphate will be found to be completely and easily soluble in an ammoniacal solution of ammonium tartrate. It is also acted on partly by caustic soda, sodium carbonate, etc.

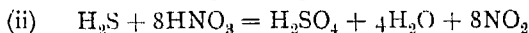
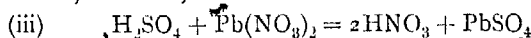
Problem 10.

1. If lead sulphide be treated with excess of hot nitric acid, a large portion of the lead will go to lead sulphate, and will be left behind, mixed up with a residue of sulphur. It may be detected by treating the residue with a warm ammoniacal solution of tartaric acid, which dissolves lead sulphate, and passing hydrogen sulphide into the solution. The action will be as follows—

(i) $$PbS + 2HNO_3 = Pb(NO_3)_2 + H_2S$$

Hydrogen sulphide, however, is readily oxidised by nitric acid, and having plenty of the latter present, a certain amount is oxidised up to sulphuric acid, thus—

(ii) $$H_2S + 8HNO_3 = H_2SO_4 + 4H_2O + 8NO_2$$

and then, of course,

(iii) $$H_2SO_4 + Pb(NO_3)_2 = 2HNO_3 + PbSO_4$$

The point, then, to be remembered is that if we wish to avoid this formation of sulphuric acid, we must give the

hydrogen sulphide formed in (i) a chance to escape, and this is done by avoiding an excess of nitric acid, as in method (*c*). If this is done carefully, the residue, if any, will be very small, and will consist of sulphur only, the lead forming lead nitrate.

If method (*b*) is used, then a certain amount of lead sulphate will be formed, but less than with method (*a*).

Now in Group II, Qualitative Analysis, mercuric sulphide is separated from lead sulphide, etc., by treating with nitric acid, in which mercury sulphide is insoluble. If, however, excess of nitric acid is at once added to the mixed sulphides, some of the lead will dissolve as lead nitrate, and some will be left as lead sulphate, mixed up with the residue of mercuric sulphide. This is undesirable for two reasons.

(*a*) It involves an additional separation, as the lead is partly in the residue and partly in the filtrate.

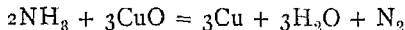
(*b*) Traces of lead (such as one gets in some commercial metals, etc.) may be missed, the amount being insufficient to be detected in Group I, and since it will form lead sulphate as above, it will also be missed in the *filtrate*, where it is generally separated as the sulphate in the usual way.

By dissolving the mixed sulphides according to method (*c*), however, it will all go to the nitrate and will be found in the filtrate by the usual method.

NITROGEN (p. 56).

Problem 1.—*The equivalent of nitrogen.*

(*a*) The action of ammonia on red-hot copper oxide is—

$$2NH_3 + 3CuO = 3Cu + 3H_2O + N_2$$

The copper oxide used *must* be that made by heating scrap copper. Devise an apparatus to find (*a*) the amount of reduction, (*b*) the volume of nitrogen, from the above reaction. Obviously the weight of ammonia need not be known.

Apparatus—

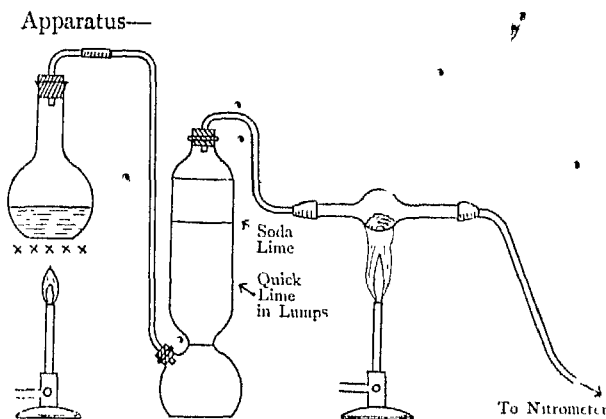



FIG. 16.

The ammonia is prepared by gently warming a little ·880 ammonia as shown. Take a weight of copper oxide that will give a volume of nitrogen rather less than the total capacity of the nitrometer. The nitrometer to be used is the one that is used in the determination of nitrogen in an organic substance by Dumas' method. Sweep all the air out of the apparatus by a stream of ammonia (the mercury trap in the nitrometer, which contains water, will prevent sucking back owing to the solubility of the ammonia). Then heat the oxide.

When the copper oxide is reduced, see that all the water is driven out of the bulb tube, and allow the copper to cool with a stream of ammonia still passing through. When cold, remove the nitrometer, replace the ammonia in the tube by a stream of *dry* air, and weigh the copper. For a loss of weight of 8 grams, 1 gram of hydrogen will have been taken from ammonia.

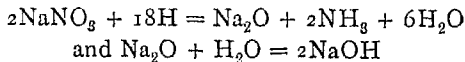
From the volume of nitrogen obtained (which will be

best measured by transferring to another nitrometer containing some dilute acid (sulphuric) to absorb any ammonia, as the ammonia solution will have a considerable vapour tension), calculate the weight of nitrogen combined with the above weight of hydrogen, and hence the equivalent. The volume of nitrogen must first, of course, be reduced to N.T.P.

(*b*) The composition by weight of ammonia being known, all we have to do to find the percentage composition of ammonium chloride is either to find the percentage of NH_3 in it by a volumetric method (see Acidimetry and Alkalimetry, Problem 3), the rest being HCl, or to find the percentage of hydrochloric acid in ammonium chloride by $\frac{N}{10}$ silver nitrate (see Problem 1 under $\frac{N}{10}$ Silver nitrate titrations). Hence calculate the amount of nitrogen in the *molecule* of ammonium chloride (*i. e.* in the weight of ammonium chloride containing 35·5 grams of chlorine). Since this weight of nitrogen is in combination with five monovalent atoms, the equivalent will be this weight divided by 5.

Problem 2.—*Reduction of nitrates by nascent hydrogen.*

The nitrate is reduced to ammonia, which is perceived by its smell.

$$2NaNO_3 + 18H = Na_2O + 2NH_3 + 6H_2O$$
$$\text{and } Na_2O + H_2O = 2NaOH$$

Hence a method for estimating nitrates, the ammonia being distilled in steam into a known excess of normal acid. Carry out the estimation.

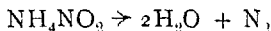
Problem 3.—*Reduction of nitric acid by zinc.*

In this case also the nitric acid is reduced to ammonia, but not quantitatively, as some nitric oxide, nitrous oxide

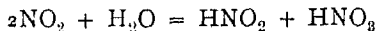
or even nitrogen may be formed as well, if the acid is not sufficiently dilute. Test for ammonia by rendering alkaline and boiling.

Problem 4.—Oxidation of nitric oxide by nitric acid.

The nitric oxide may be oxidised to the peroxide by the strong nitric acid, giving, with the very strong acid, red fuming nitric acid. With more dilute nitric acid, the presence of nitrous acid (formed by $2NO_2 + H_2O = HNO_3 + HNO_2$) may be *seen* by the solution becoming blue. With very dilute acid nothing happens, *providing that precautions are taken* to prevent the peroxide, NO_2 [formed by the nitric oxide coming into contact with the air], from dissolving in the acid. The solution in each case should be neutralised and tested for a nitrite and a nitrate. First test for a nitrite in the usual way, then destroy the nitrite by boiling with excess of ammonium chloride and test for a nitrate.

$$NH_4NO_2 \rightarrow 2H_2O + N_2$$

Problem 5.—Action of nitrogen peroxide on potash.

Since the peroxide NO_2 (or N_2O_4) is half way between N_2O_3 and N_2O_5 (nitr*ous* and nitr*ic* anhydrides) we should expect to get both these acids formed in equimolecular quantities, thus—

$$2NO_2 + H_2O = HNO_2 + HNO_3$$

Test for both. Break a bulb containing a weighed amount of liquid peroxide under some caustic soda solution, and estimate the nitrous acid as in Problen 10 under $\frac{N}{10}$ Permanganate estimations. It should be found that one-half of the nitrogen in the peroxide is now present as nitrous acid, HNO_2, therefore the other half is present as nitric acid.

Problem 7.—Hydroxylamine and hydrazine.

The substances supplied were hydrazine hydrochloride and hydroxylamine hydrochloride. Both will be found to be powerful reducing agents, reducing silver salts to silver, mercuric salts to mercury, bismuth salts to bismuth, ferric salts to ferrous, and copper salts to cuprous oxide. See if either of them possesses oxidising properties. Which will it be, if this is the case? See Problem 10.

Problem 8.—Reduction of nitric acid.

The hydrogen from metallic tin and dilute hydrochloric acid reduces nitric acid partly to hydroxylamine and partly to ammonia. Hence the filtrates from the precipitate of stannous sulphide will contain a mixture of the hydrochlorides of these two bases. The former is soluble in alcohol, the latter almost insoluble. Hence the separation. Hydroxylamine will reduce sodium stannite to tin, hence on adding caustic soda to a little of the original solution, we get a black precipitate of metallic tin. Other tests for hydroxylamine are given in Problem 7.

Problem 9.—Oxidation of ammonia by air.

The apparatus is as shown.

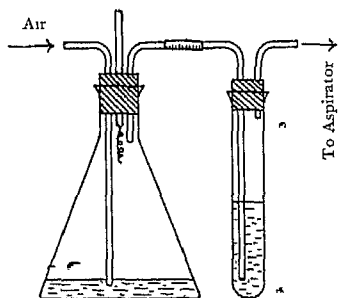



FIG. 17.

The flask contains a little ·880 ammonia, the boiling tube potash.

Set the aspirator working, remove the cork, heat the platinum spiral red-hot, and quickly put the cork back. The air-stream should be regulated to give the best glow on the wire. The exit tube should

be close to the spiral, so that the products of oxidation are carried off at once. The *possible* oxidation products are hydroxylamine, nitrous and nitric acids, oxides of nitrogen, and nitrogen and water. After the experiment, each of these (except the last-named) should be tested for in the potash solution; potassium nitrite only will be found, except such *traces* of nitrate as may have been formed by oxidation of the nitrite by atmospheric oxygen.

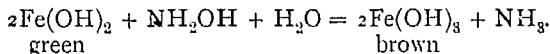
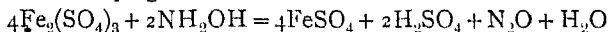
Problem 10.—*Action of hydroxylamine on iron salts.*

Hydroxylamine has one oxidising action. It will oxidise ferrous hydroxide to ferric hydroxide in alkaline solution (*i. e.* the *free base* is the oxidising agent), being itself reduced to ammonia, which can be smelt when the solution is warmed. On again acidifying, the usual reducing properties of hydroxylamine salts are seen, and the resulting ferric salt is at once reduced to the ferrous state again.

In alkaline solution—

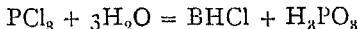
$$\underset{\text{green}}{2Fe(OH)_2} + NH_2OH + H_2O = \underset{\text{brown}}{2Fe(OH)_3} + NH_3.$$

On acidifying—

$$4Fe_2(SO_4)_3 + 2NH_2OH = 4FeSO_4 + 2H_2SO_4 + N_2O + H_2O$$

PHOSPHORUS (p. 58).

Problem 1.—*Equivalent of phosphorus.*

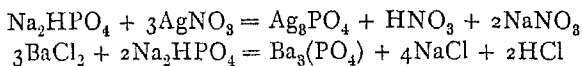
Some phosphorous chloride, PCl_3, is weighed out in a sealed bulb tube, which is then broken under 200 c.c. of water in a large beaker. (·25 – ·4 gram will be enough.)

$$PCl_3 + 3H_2O = BHCl + H_3PO_3$$

The phosphorous acid is oxidised to phosphoric by adding some nitric acid and warming gently. (Why?) The hydrochloric acid is then precipitated as silver chloride, washed, dried, and weighed in the usual way. Calculate

the weight of phosphorus that combines with 35·5 grams of chlorine.

Problem 2.—Reactions of the phosphoric acids.

Ortho-phosphates give a yellow ppt. with silver nitrate, and a white precipitate with barium chloride, in neutral solution.

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + HNO_3 + 2NaNO_3$$
$$3BaCl_2 + 2Na_2HPO_4 = Ba_3(PO_4) + 4NaCl + 2HCl$$

Pyrophosphates give a white precipitate with silver nitrate and with barium chloride. The solution of the free acid does *not* coagulate albumen. To carry out the albumen test, acidify the alkali salt with acetic acid before adding the albumen.

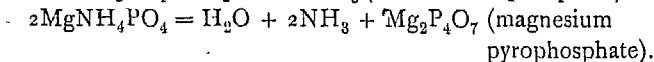
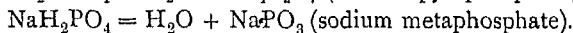
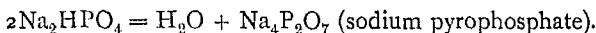
Metaphosphates give white precipitates with silver nitrate and barium chloride, and the free acid coagulates albumen.

Hence, to distinguish between pyro-, meta- and orthophosphates, add silver nitrate to the neutral sodium salt solution. If a yellow precipitate, it is an orthophosphate. If a white precipitate, to a further portion add dilute acetic acid and some dilute albumen solution. If it coagulates it is a metaphosphate; if not, a pyrophosphate.

You are now in a position to try Problems 3, 4 and 5.

Problem 3.—Action of heat on various phosphates.

The reactions are as follows—

$$2Na_2HPO_4 = H_2O + Na_4P_2O_7 \text{ (sodium pyrophosphate).}$$
$$NaH_2PO_4 = H_2O + NaPO_3 \text{ (sodium metaphosphate).}$$
$$2MgNH_4PO_4 = H_2O + 2NH_3 + Mg_2P_4O_7 \text{ (magnesium pyrophosphate).}$$

How will you test this?

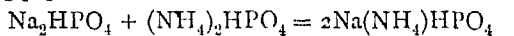
Problem 4.—Microcosmic salt.

Take two *equal* volumes of the phosphoric acid. Neutralise one with sodium carbonate, the other with ammonia (litmus).

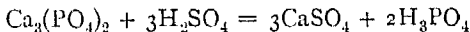
This gives equimolecular proportions of Na_2HPO_4 and $(NH_4)_2HPO_4$. Mix them together, filter if necessary, and crystallise. Drain on the pump, and dry quickly between blotting-paper.

$$Na_2HPO_4 + (NH_4)_2HPO_4 = 2Na(NH_4)HPO_4$$

Action of heat—

$$NaNH_4HPO_4 = NH_3 + H_2O + NaPO_3$$

Problem 5.—Phosphoric acid and phosphates from bone-ash.

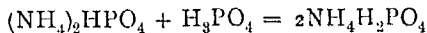
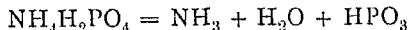
Take quantities of the bone-ash and concentrated H_2SO_4 in the proportions required by the equation, using *rather* more acid than required.

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4$$

Add the sulphuric acid to about eight times its volume of water. Raise to the boil in a porcelain basin, and add the bone-ash gradually. When all is added, put in a little more water (to keep up the volume), and boil for several minutes. Cool, filter by suction, and wash the residue with several small quantities of cold water. Evaporate the filtrate in a porcelain basin on a sand-bath till no more fumes of H_2SO_4 are evolved. Allow to cool, take up with water, and boil for a few minutes. Filter if necessary. It is now ready for use.

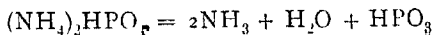
To make ammonium dihydrogen phosphate, $(NH_4)H_2PO_4$, take two equal volumes of the acid, neutralise one with ammonia (litmus), and add the other. Crystallise.

$$(NH_4)_2HPO_4 + H_3PO_4 = 2NH_4H_2PO_4$$

Action of heat—

$$NH_4H_2PO_4 = NH_3 + H_2O + HPO_3$$

To make $(NH_4)_2HPO_4$ neutralise phosphoric acid with ammonia (litmus).

Action of heat—

$$(NH_4)_2HPO_4 = 2NH_3 + H_2O + HPO_3$$

Problem 6.—*Action of phosphorus on alkalis.*

When the barium compound obtained by this process is heated, water and phosphine are evolved, and a pyrophosphate will be left. Confirm this.

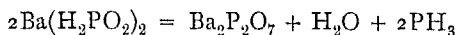
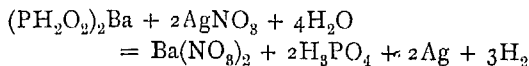
Evidently then it is the barium salt of a lower acid of phosphorus than phosphoric, and on being heated part is oxidised at the expense of the other part. The lower acids of phosphorus are phosphorous and hypophosphorous acids (H_3PO_3 and H_3PO_2).

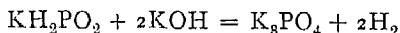
Barium phosphite is insoluble in water (like barium phosphate), and this substance will be found to be a much more powerful reducing agent than a phosphite is. Hence we conclude that it is barium hypophosphite, $Ba(H_2PO_2)_2$.

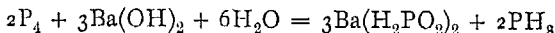
On ignition—

$$2Ba(H_2PO_2)_2 = Ba_2P_2O_7 + H_2O + 2PH_3$$

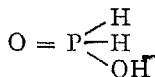
Silver nitrate is reduced to metallic silver.

$$(PH_2O_2)_2Ba + 2AgNO_3 + 4H_2O$$
$$= Ba(NO_3)_2 + 2H_3PO_4 + 2Ag + 3H_2$$

Mercuric chloride is reduced to metal, and concentrated potash oxidises it to phosphate, being itself reduced, thus—

$$KH_2PO_2 + 2KOH = K_3PO_4 + 2H_2$$

The formation of the substance takes place thus—

$$2P_4 + 3Ba(OH)_2 + 6H_2O = 3Ba(H_2PO_2)_2 + 2PH_3$$

The free acid is found to be *monobasic*, only one of the three H atoms being replaceable.

Hence it is usually written

$$O = P \begin{cases} H \\ H \\ OH \end{cases}$$

to indicate this. The hydrogen of the hydroxyl group is the acid hydrogen.

Problem 7.—Reduction of copper salts by hypophosphorous acid.

The substance produced by the action of hypophosphorous acid on copper sulphate will be found to behave as follows—

(*a*) Dissociates on heating into hydrogen, which is evolved, and metallic copper. Unless care is taken to prevent the hot copper coming into contact with air, copper oxide may be formed.

(*b*) With strong hydrochloric acid hydrogen is evolved, and on pouring the solution into water, cuprous chloride is precipitated (soluble in strong hydrochloric acid).

Hence the substance is cuprous hydride.

Problem 8.—Reducing powers of phosphorous and hypophosphorous acids.

Phosphorous acid will be found to do *most* of the reductions that the hypophosphorous acid will do, only more slowly, and often the aid of heat is required.

Examples.—Strong sulphuric is reduced to sulphur dioxide on warming by both acids.

Silver nitrate is reduced to metallic silver at once by hypophosphorous acid, but with phosphorous acid a white precipitate of silver phosphite is produced *first* (in *neutral* solutions). This goes to metallic silver almost at once in strong solutions, but in dilute ones only on warming.

Mercuric chloride is reduced at once to the metal by the lower acid, but with phosphorous acid the reduction goes slowly in the cold to mercurous chloride, and then to mercury, if excess of the acid is present, *in hot solution only*.

Phosphorous acid will not reduce copper salts even to metal, whereas hypophosphorous acid reduces them to copper *hydride*.

ARSENIC (p. 62).

Problem 1.—*The equivalent of arsenic.*

Sufficient details have been given with the problem.

Problem 2.—*Action of arsenious acid on nitric acid.*

Strong nitric acid on arsenious oxide gives us a deep brown gas that condenses to a blue liquid in the freezing mixture. When dissolved in ice-cold alkalis it forms nitrites, and with water (air-free) it gives nitrous acid. Hence it is nitrous anhydride, N_2O_3. In the gaseous state it has been shown to be largely dissociated into NO and NO_2 (equal volumes of each).

The residue left after the action of the acid on arsenious oxide is found to give sodium arsen*ate* when evaporated quite dry, and neutralised by sodium carbonate.

Hence we see that the $As_2O_3 \rightarrow As_2O_5$, and the $HNO_3 \rightarrow HNO_2$ (*i.e.* $N_2O_3 + H_2O$).

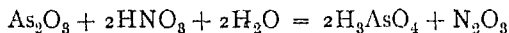
$\therefore$ As_2O_3 requires $2O$, supplied by $2HNO_3$, and the equation therefore is—

(*a*) $As_2O_3 + 2HNO_3 = As_2O_5 + H_2O + N_2O_3$

The As_2O_5 forms arsenic acid with the water that is of course present.

(*b*) $As_2O_5 + 3H_2O = 2H_3AsO_4$

The complete equation, therefore, by adding (*a*) and (*b*), is—

$$As_2O_3 + 2HNO_3 + 2H_2O = 2H_3AsO_4 + N_2O_3$$

The arsenic acid on being heated to about 275° C. parts with water, leaving the anhydride As_2O_5. On further heating, $As_2O_5 = As_2O_3 + O_2$.

If metallic arsenic is available, we have here a method of finding the equivalent of pentavalent arsenic, by turning it to As_2O_5 by the direct action of strong HNO_3

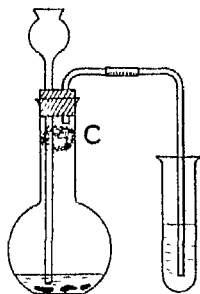
Problem 3.—Magnesium ammonium arsenate.

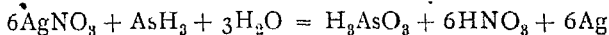
Details have been given under Magnesium, Problem 4. The magnesium ammonium arsenate may be prepared from the arsenic acid obtained in Problem 2.

Problem 4.—Action of arsine on silver nitrate.

Set up the apparatus shown, to prepare small quantities of arsine, AsH_3. (C = cotton wool.)

FIG. 18.

Passed into $AgNO_3$ solution, we get a dark precipitate, which on filtering and washing is shown to be metallic silver. The filtrate is found to be strongly acid. On neutralising and testing with silver nitrate, we get a yellow precipitate of silver arsen*ite*, showing that the arsine has been oxidised to the state of arsenious acid (As_2O_3).

Tests for a nitrate also show that plenty of nitric acid was left. Hence the action of arsine on *dissolved* silver nitrate is—

$$6AgNO_3 + AsH_3 + 3H_2O = H_3AsO_3 + 6HNO_3 + 6Ag$$

The points to notice about this are that the nitric acid is *not reduced*, although the arsenic has been oxidised. The hydrogen of the arsine has partly taken the place of the silver in the silver nitrate, and the water has supplied the rest of the necessary hydrogen, the arsenic being oxidised to arsenious acid by the oxygen from this water.

ANTIMONY (p. 63).

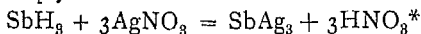
Problem 1.—Equivalents of antimony.

Sufficient details are given with the problem.

Problem 2.—Action of stibine on silver nitrate solution.

The details for the performance of the experiment are similar to those for the corresponding problem under Arsenic.

A black precipitate will be formed, which on analysis proves to be a compound of silver and antimony. Neither silver nor antimony should be found in the filtrate, but only free nitric acid. The formula to be expected for silver antimonide would be $SbAg_3$. If this is the case, the action is simply—

$$SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3^*$$

This can obviously be very easily settled in the following manner—

(*a*) The nitric acid resulting from a known amount of silver nitrate (*i. e.* a measured volume of $\frac{N}{10}$ silver nitrate solution) can be titrated after filtering off the precipitate.

(*b*) The percentage composition of the precipitate can be found by determining the percentage of silver in it by dissolving the dried and weighed precipitate in strong nitric acid (1 : 1), diluting, and titrating the silver by means of $\frac{N}{10}$ thiocyanate. The result should agree approximately with that demanded by the formula.

BISMUTH (p. 64).

Problem 1.—The equivalent of bismuth

Carry out the experiment in a small hard-glass flask of 50 c.c capacity, or in a large porcelain crucible.

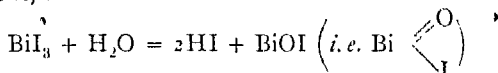
Problem 2.—Properties of bismuth iodide.

At first a black precipitate of bismuth iodide, BiI_3, forms. This dissolves in excess of potassium iodide to form an orange solution, which contains the double iodide $KBiI_4$.

* This reaction will only be complete if the nitric acid be at any rate partly neutralised. This should be done by gradually adding $\frac{N}{10}$ ammonia as the action proceeds, finally finishing with phenol phthaleïn.

On gradually adding water to this, we get examples of both kinds of hydrolytic dissociation. First, the double salt dissociates into its constituents, $KBiI_4 \rightarrow KI + BiI_3$.

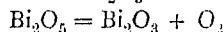
The bismuth iodide is then hydrolysed just like bismuth chloride is, thus—

$$BiI_3 + H_2O = 2HI + BiOI \left(i.e.\ Bi \begin{matrix} \diagup O \\ \diagdown I \end{matrix} \right)$$

forming basic bismuth iodide, a red powder.

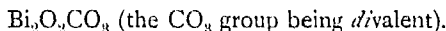
N.B.—Do not confuse this with bismuth hypoiodite which, *if it existed*, would obviously be $Bi(OI)_3$.

Problem 3.—*Oxidation of bismuth by halogens.*

The precipitate is bismuth pentoxide, Bi_2O_5, often known as bismuthic acid. On heating it gives off oxygen, and goes back to the yellow trioxide Bi_2O_3.

$$Bi_2O_5 = Bi_2O_3 + O_2$$

Problem 4.—*Bismuth carbonate.*

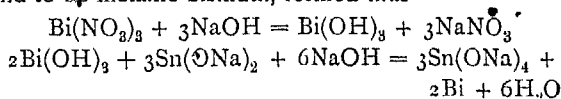
$Bi_2(CO_3)_3$ does *not* exist. From the analogy of the hydrolysis of the chloride and iodide, which form BiOCl and BiOI with water, we should perhaps expect an analogous carbonate, which would be, of course,

$Bi_2O_2CO_3$ (the CO_3 group being *di*valent).

This substance is actually formed, as the determination of the carbon dioxide in the carefully washed and dried precipitate will show.

Problem 5—*Reduction of bismuth by sodium stannite.*

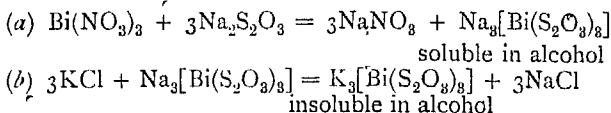
Sodium stannite, $Sn(ONa)_2$, is a reducing agent, being ready to pass over into sodium stannate, $Sn(ONa)_4$, in the presence of excess of alkali. The black precipitate will be found to be metallic bismuth, formed thus—

$$Bi(NO_3)_3 + 3NaOH = Bi(OH)_3 + 3NaNO_3$$

$$2Bi(OH)_3 + 3Sn(ONa)_2 + 6NaOH = 3Sn(ONa)_4 + 2Bi + 6H_2O$$

Problem 6.—A test for potassium.

The reactions are as follows—

(*a*) $Bi(NO_3)_3 + 3Na_2S_2O_3 = 3NaNO_3 + Na_3[Bi(S_2O_3)_3]$
soluble in alcohol

(*b*) $3KCl + Na_3[Bi(S_2O_3)_3] = K_3[Bi(S_2O_3)_3] + 3NaCl$
insoluble in alcohol

The precipitate should be washed with alcohol and analysed qualitatively. This is Carnot's reaction for potassium.

OXYGEN (p. 65).

Problem I.

Sufficient details are given with the problem.

Problem 2.—Classification of peroxides.

The peroxides of manganese and lead give off chlorine with hot strong hydrochloric acid, but not in the cold. Manganese dioxide goes into solution in cold strong hydrochloric acid, giving a dark olive-green solution, which liberates chlorine on heating:—

Possibly—

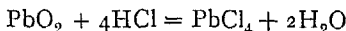
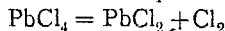
$$MnO_2 + 4HCl = 2H_2O + MnCl_4$$

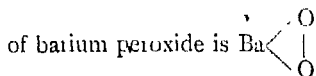
and then— $$MnCl_4 = MnCl_2 + Cl_2$$

This points to the formula $Mn\begin{smallmatrix}\nearrow O \\ \searrow O\end{smallmatrix}$ for manganese dioxide.

Lead tetrachloride ($PbCl_4$) has been prepared; it is very unstable, and at the ordinary temperature breaks up into $PbCl_2 + Cl_2$. Hence probably—

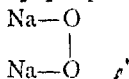
$$PbO_2 + 4HCl = PbCl_4 + 2H_2O$$

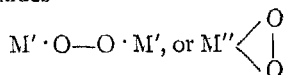
and then— $$PbCl_4 = PbCl_2 + Cl_2$$

pointing to the formula $Pb\begin{smallmatrix}\nearrow O \\ \searrow O\end{smallmatrix}$ for lead dioxide

With barium peroxide, however, strong hydrochloric acid liberates **oxygen**, and dilute hydrochloric acid cold forms hydrogen peroxide. No compounds of barium are known in which barium is tetravalent, hence the probable formula of barium peroxide is $Ba\langle\begin{smallmatrix}O\\|\\O\end{smallmatrix}$

$$BaO_2 + 2HCl = BaCl_2 + H_2O + O$$ (or H_2O_2 if the acid is dilute and cold).

Similarly, sodium peroxide gives oxygen or hydrogen peroxide, even with water alone.

Hence the formula of Na_2O_2 is probably—

$$\begin{matrix}Na—O\\ \quad\;\,|\\ Na—O\end{matrix}$$

These peroxides illustrate the two different types of peroxides that are met with. One type gives off chlorine with strong hydrochloric acid, and the other type gives off oxygen. The type that gives off oxygen can be made to yield hydrogen peroxide by having the acid dilute and cold. The only possible formula for hydrogen peroxide is $H \cdot O—O \cdot H$, and hence the reason for writing the corresponding peroxides—

$$M' \cdot O—O \cdot M', \text{ or } M''\langle\begin{smallmatrix}O\\|\\O\end{smallmatrix}$$

On the other hand, none of the peroxides which give chlorine with strong hydrochloric acid can be made to yield hydrogen peroxide, and in every case there is either evidence of a higher valency existing in the metal (as in the case of manganese), or the compound in which this higher valency exists is actually known (as in the case of lead).

Hence the first action of the acid is to form the tetrachloride, which breaks up into the lower chloride or chlorine.

The impossibility of getting hydrogen peroxide from them points to the fact that the oxygen atoms are not united to each other in this type of peroxide.

Problem 4.—Reactions of hydrogen peroxide.

The reactions of hydrogen peroxide can be classified as (*a*) oxidations, (*b*) reductions, (*c*) catalytic decompositions.

It will oxidise most reducing agents, such as hydriodic acid, ferrous salts, etc. It will also oxidise metallic sulphides to sulphates, and ferrocyanides to ferricyanides, and it oxidises chromic acid to some higher acid possessing a blue colour (soluble in ether) which is probably $HCrO_4$ [or $H_2Cr_2O_8$], analogous to persulphuric acid.

It reduces several strong oxidising agents, the action being a mutual reduction, so to speak ; an atom of oxygen from the peroxide and one from the other oxidising agents pairing off to form a molecule. In this way acid permanganates and silver oxides are reduced.

It is decomposed catalytically, in the cold, by platinum black, silver leaf, "molecular" silver, and metallic mercury.

Problem 5.—Action of oxygen on the luminous gas-flame.

The oxygen is best delivered from a gas-holder, so that the stream can be regulated as required. Failing this, a football bladder with a screw pinch-cock on the nozzle answers excellently. If generated from chlorate and manganese dioxide, a "by-pass" arrangement may be easily devised, and the stream regulated by a screw pinch-cock. A suggestion is given in the figure. (B = By-pass.)

When the stream of oxygen is slowly admitted, the luminous flame at first shortens and becomes more intensely luminous. As the stream increases, the luminosity slowly disappears, and the flame becomes non-luminous, smaller, and very hot. The explanation is probably that the heavy

hydrocarbons, whose incandescence causes the luminosity of the flame, are raised in temperature by the admittance of oxygen, owing to the increased temperature of the flame. When more oxygen is admitted, however, they are burnt up

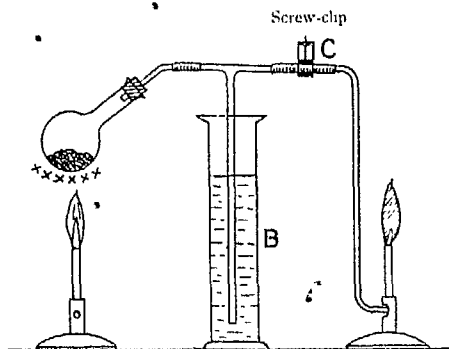



FIG. 19.

at once, and no free particles of carbon at all will exist in the flame.

Problem 6.—Oxidising powers of electrolytic oxygen.

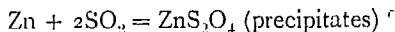
The oxidising powers of "electrolytic" oxygen at the anode are considerable. The substances given will be oxidised respectively to (*a*) CO_2; (*b*) CuO (forming $CuSO_4$ with the acid); (*c*) Fe_2O_3, with probably a little sodium ferrate (violet colour); (*d*) permanganate acid (*i.e.* Mn_2O_7), shown by the purple colour; (*e*) PbO_2. In each case note that the highest possible oxidation product is formed.

If a piece of palladium is available, saturate it with hydrogen (by making it the *cathode* in the electrolysis of dilute sulphuric acid for a short time), and then make it the *anode*. The oxygen will be found to oxidise some of the hydrogen to hydrogen peroxide (chromic acid test).

SULPHUR (p. 67).

Problem 3.—Reduction of sulphurous acid.

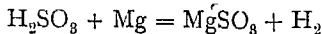
Providing that no sulphuric acid is formed by oxidation, the zinc goes into solution without the evolution of any gas, thus—

$$Zn + 2SO_2 = ZnS_2O_4 \text{ (precipitates)}$$

This is zinc hyposulphite, and it is not yet certain whether the free acid has the formula HSO_2 or $H_2S_2O_4$. It has never been isolated. It is a powerful reducing agent, being oxidised first to sulphurous and then to sulphuric acid.

With dilute hydrochloric acid, etc., the solution turns yellow, then brown, and slowly deposits sulphur, whilst sulphur dioxide is evolved at the same time. It may be distinguished from thiosulphate by the slowness of the reaction and by the initial colour change, also by titrating with iodine, which oxidises it to sulphuric acid: the amount of iodine required is *far more* than if the substance was a thiosulphate. It is, moreover, a powerful reducing agent, solutions of mercuric chloride and silver nitrate being reduced to the metal, whilst Fehling's solution is reduced to cuprous oxide and perhaps copper.

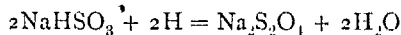
If the sodium salt of this acid is exposed to air in the moist state, it forms $Na_2S_2O_5,H_2O$, which is the sodium "metabisulphite" used in photography.

The action of sulphurous acid on magnesium is the normal action.

$$H_2SO_3 + Mg = MgSO_3 + H_2$$

Problem 3a.—Reduction of sulphurous acid by electrolytic hydrogen.

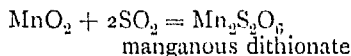
A small H-shaped electrolytic cell, with platinum electrodes, is suggested. The cathode liquid can then be

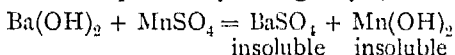
pipetted off. The action of electrolytic hydrogen on a sulphite (or sulphurous acid) is to reduce it to the hyposulphite, the sodium salt of which crystallises out under favourable circumstances.

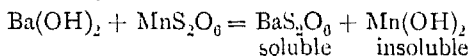
$$2NaHSO_3 + 2H = Na_2S_2O_4 + 2H_2O$$

A solution of this salt will react in a similar way to the solution of zinc hyposulphite already obtained in Problem 3.

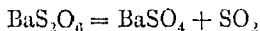
Problem 4.—*Action of sulphur dioxide on manganese dioxide.*

In the *cold*, the main reaction that takes place is the following—

$$MnO_2 + 2SO_2 = Mn_2S_2O_6$$
manganous dithionate

If the temperature be allowed to rise, the sulphate is formed, but by cooling very little sulphate is formed. Any that is formed is separated by adding baryta, thus—

$$Ba(OH)_2 + MnSO_4 = BaSO_4 + Mn(OH)_2$$
insoluble insoluble

The soluble barium salt of the other product is formed at the same time, thus—

$$Ba(OH)_2 + MnS_2O_6 = BaS_2O_6 + Mn(OH)_2$$
soluble insoluble

It crystallises with two molecules of water of crystallisation, $BaS_2O_6,2H_2O$. Hence on evaporating, the *barium* salt instead of the manganese one is obtained. On heating the dry salt, it gives off water of crystallisation and then sulphur dioxide, and barium sulphate is left.

$$BaS_2O_6 = BaSO_4 + SO_2$$

Free dithionic acid is unstable when warmed, even in dilute solution, so that on acidifying the barium dithionate solution with hydrochloric acid, and heating, we get a precipitate of barium sulphate, and sulphur dioxide is evolved.

The dithionate solution will be found to reduce iodine solution, mercuric chloride and silver nitrate solutions, Fehling's solution, etc. Its quantitative composition may be found by weighing the barium sulphate left when the solution of the barium salt (allowing for the assumed percentage of water of crystallisation) is acidified with hydrochloric acid and boiled for some time. Also the equation

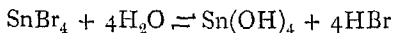
$$BaS_2O_6,2H_2O = BaSO_4 + SO_2 + 2H_2O \text{ (by ignition)}$$

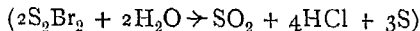
can easily be confirmed.

Problem 5.—*Action of bromine on metallic sulphides.*

Lead bromide will be found in the boat at the end of the experiment. A thick, yellow liquid will be evolved, which is *not* molten sulphur, for it remains liquid on cooling It is decomposed by the water to give sulphur, sulphur dioxide, and hydrobromic acid, and is sulphur bromide, S_2Br_2. (Compare S_2Cl_2, Problem 3, under $\frac{N}{10}$ Silver nitrate.) The apparatus suggested is shown in Fig. 9.

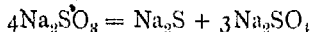
The action on stannic sulphide, SnS_2, is precisely similar, except that stannic bromide, $SnBr_4$, is produced, which of course is volatile (like $SnCl_4$), and goes off into the water in the wash-bottle. It is there hydrolysed, giving a precipitate of stannic acid, $Sn(OH)_4$. Thus—

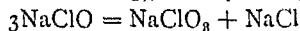
$$SnBr_4 + 4H_2O \rightleftharpoons Sn(OH)_4 + 4HBr$$

the reaction of course being somewhat reversible. The sulphur dioxide produced by the sulphur bromide acting on the water

$$(2S_2Br_2 + 2H_2O \rightarrow SO_2 + 4HCl + 3S)$$

may reduce some of the stannic bromide to stannous. Hence look for both stannous and stannic tin in the solution in the wash-bottle.

Problem 6.—Action of heat on sodium sulphite.

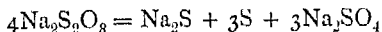
Sodium sulphite on heating strongly is oxidised, at its own expense, to sodium sulphate, part being therefore reduced to sodium sulphide.

$$4Na_2SO_3 = Na_2S + 3Na_2SO_4$$

Extract the heated mass with water. It should be completely soluble. Test for sulphide and sulphate. This class of action, or self-oxidation, is well exemplified by the sulphites (see under Silver, Problem 3), and by the hypochlorites, etc.

$$3NaClO = NaClO_3 + NaCl$$

Also by the manganates in acid solution. (See under Manganese, Problem 4*a*.)

Problem 7.—Action of heat on sodium thiosulphate.

Sodium thiosulphate undergoes self-oxidation on being heated *strongly*, thus—

$$4Na_2S_2O_3 = Na_2S + 3S + 3Na_2SO_4$$

Look for this sulphur being evolved. It will, of course, be seen best if the heating be carried out in a test-tube of hard glass, as the sulphur will then sublime on the cool part of the tube.

Problem 8.—Preparation of potassium persulphate.

If the anions [which in this case, the solution being strong, are (HSO_4)] are *crowded together*, by the use of a *small anode*, they combine [instead of producing sulphuric acid and oxygen] to form persulphuric acid, $H_2S_2O_8$. The potassium salt of this acid is fairly insoluble, and crystallises out after some time. It will be found to be a very powerful oxidising agent, being reduced, of course, to sulphuric acid. Try its action on solutions of permanganate, hydrogen peroxide, ferrous salts, stannous salts, sulphurous acid, potassium iodide, etc.

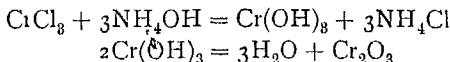
CHROMIUM (p. 71).

Problem 1.—*To find the equivalent.*

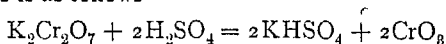
Dissolve a weighed amount of chromium in hot nitric acid (1 : 1). Evaporate dry, and ignite to turn the nitrate to the oxide Cr_2O_3. Note that chromium may be "passive" to nitric acid, like iron is.

Problem 2.—*Preparation of chromic oxide.*

The hydroxide is precipitated by the addition of ammonium chloride and ammonia. Boil for several minutes, allow to settle; filter, wash, dry, and ignite the precipitate in the usual way.

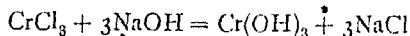
$$CrCl_3 + 3NH_4OH = Cr(OH)_3 + 3NH_4Cl$$
$$2Cr(OH)_3 = 3H_2O + Cr_2O_3$$

Problem 3.—*Preparation of chromic anhydride.*

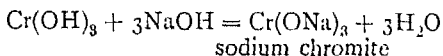
The action of strong sulphuric acid on potassium dichromate is as follows—

$$K_2Cr_2O_7 + 2H_2SO_4 = 2KHSO_4 + 2CrO_3$$

About twice as much sulphuric acid is used as is demanded by the above equation, partly to enable the bisulphate to crystallise better, and partly to cause the anhydride, which is extremely soluble in water, to crystallise out on further concentration. After adding the sulphuric acid *cautiously* to a hot strong solution of the dichromate, stand overnight, decant from the crystals of bisulphate, add a little more sulphuric acid, and evaporate on a *water-bath* (Why?) till the surface is covered with crystals of the anhydride. Allow to cool. Filter through glass-wool, and wash with strong nitric acid, which can be got rid of by heating the crystals gently on a sand-bath to about 150° C. (not more).

Problem 4.—Oxidation of chromic salts to chromates.

On adding caustic soda to a chromic salt, the action is—

$$CrCl_3 + 3NaOH = Cr(OH)_3 + 3NaCl$$

Chromic hydroxide behaves towards soda and potash like a *very feeble* acid, and hence on adding more alkali

$$Cr(OH)_3 + 3NaOH = \underset{\text{sodium chromite}}{Cr(ONa)_3} + 3H_2O$$

(*a*) This forms a green solution. On boiling it is hydrolysed, and the above action takes place from right to left, the hydroxide being reprecipitated. Sodium aluminate, on the other hand, is not so hydrolysed. Hence to separate chromium from aluminium, we add soda to the solution till the precipitates redissolve. Then dilute somewhat, and boil. Filter whilst hot.

(*b*), (*c*), (*d*), etc. Sodium chromite is oxidised to sodium chromate by various oxidising agents, thus:—

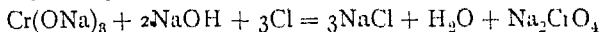
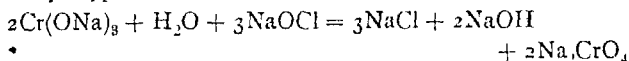
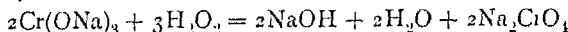
By Halogens—

$$Cr(ONa)_3 + 2NaOH + 3Cl = 3NaCl + H_2O + Na_2CrO_4$$

By Hypochlorites, etc.—

$$2Cr(ONa)_3 + H_2O + 3NaOCl = 3NaCl + 2NaOH + 2Na_2CrO_4$$

By Peroxides—

$$2Cr(ONa)_3 + 3H_2O_2 = 2NaOH + 2H_2O + 2Na_2CrO_4$$

The chromate may be tested for by first acidifying with ACETIC acid and then adding lead acetate in the usual way.

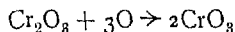
Problem 5.—Oxidation of a chromium salt in neutral solution.

Freshly precipitated manganese dioxide $\left(Mn\begin{matrix} \diagup OH \\ = O \\ \diagdown OH \end{matrix}\right)$ got by oxidising manganous hydrate, $Mn(OH)_2$, with bromine water, and washing, is warmed with a solution of a chromic

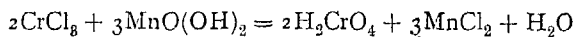
salt. Note that the reaction, which is neutral at first (or at any rate only weakly acid), becomes strongly acid, the solution turns yellow, and both a manganous salt and chromic acid can be found in the filtrate by suitable tests (*e.g.* for manganous salt add ammonia and bromine water). Brown $MnO(OH)_2$ is precipitated. For chromic acid, render alkaline with ammonia, then acid with acetic acid, and add some lead acetate. Yellow lead chromate is precipitated.

Hence the action must be thus—

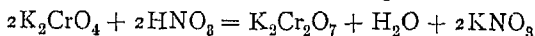
The chromium has been oxidised from the state of Cr_2O_3 to the state of CrO_3. This requires three atoms of oxygen for two atoms of chromium, thus—

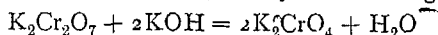
$$Cr_2O_3 + 3O \rightarrow 2CrO_3$$

The manganese has been reduced from the state of MnO_2 to the state of MnO, and hence three molecules of MnO_2 are wanted for one molecule of Cr_2O_3.

Hence equation—

$$2CrCl_3 + 3MnO(OH)_2 = 2H_2CrO_4 + 3MnCl_2 + H_2O$$

Problem 6.—*The chromates of potassium.*

On acidifying potassium chromate solution with *any* acid (except very weak ones, like carbonic), potassium dichromate is formed, observable by the colour change of the solution.

$$2K_2CrO_4 + 2HNO_3 = K_2Cr_2O_7 + H_2O + 2KNO_3$$

If potassium dichromate solution is made alkaline it goes back to chromate, also observable by colour change.

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O$$

The amounts of each in a mixture of the chromate and dichromate can be found approximately by the following methods—

(*a*) Render strongly alkaline with ammonia a solution of a weighed quantity of the mixture in a porcelain basin,

and evaporate dry on a sand-bath. Repeat, and weigh the product.

$$K_2Cr_2O_7 + 2NH_4OH = K_2CrO_4 + (NH_4)_2CrO_4 + H_2O$$

Hence, for every molecule of potassium dichromate present, we see there will be a gain in weight of—

$$\begin{array}{llllll} (NH_4)_2O. \quad \text{Thus:} & K_2Cr_2O_7 & \rightarrow & K_2CrO_4 & + & (NH_4)_2CrO_4 \\ 52 & 294 & \rightarrow & 194 & + & 152 \quad = 346 \end{array}$$

Hence a gain in weight of 52 grams means that 294 grams of $K_2Cr_2O_7$ were present.

(*b*) By adding excess of nitric acid to the solution of a weighed portion of the mixture, and evaporating dry on a sand-bath. Here

$$\begin{array}{ll} 2K_2CrO_4 + 2HNO_3 = H_2O + K_2Cr_2O_7 + 2KNO_3 \\ 2 \times 194 = 388 \qquad\qquad 294 \times 2(140) = 574 \end{array}$$

Here it will be seen that for every $2K_2CrO_4$ present there is a gain of N_2O_5, or, expressed in grams, a gain of 108 grams represents $2 \times 194 = 388$ grams of potassium chromate in the mixture.

Both methods may be tried, and the mean value taken.

Otherwise, on titration with standard alkali, the change of colour from orange to yellow may be taken as the end of the conversion of dichromate into chromate. The end-point, however, is not very sharp, even if the alkali be fairly strong. Still, an approximate result can be arrived at thus. The alkali should be at least twice normal.

Problem 7.—Reduction of chromates to chromic salts.

The experiments performed here show that CrO_3 is very readily reduced to Cr_2O_3 in acid solution—

$$(a) \quad K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$$

(*b*) $K_2Cr_2O_7 + 3H_2S + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$

(*c*) $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 = K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

(*d*) $K_2Cr_2O_7 + 7H_2SO_4 + 6KI = 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2$

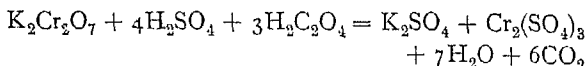
(*e*) As for KI.

(*f*) $K_2Cr_2O_7 + 14HCl = 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$

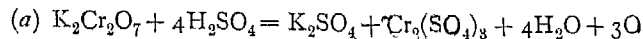
Note, however, that (*f*) only goes readily on boiling with very strong hydrochloric acid, and even then the reduction takes some time.

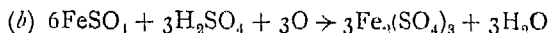
(*g*) Alcohol is oxidised to acetaldehyde. See preparation of Chrome alum (p. 18) for equation.

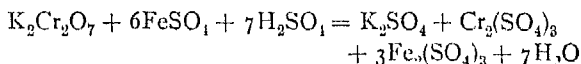
(*h*) Oxalic acid is oxidised to carbon dioxide and water.

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2C_2O_4 = K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 6CO_2$$

The above equations are all very simply arrived at by a consideration of the initial and final states of oxidation of the chromium. The student should not attempt to learn them by heart, but should be able to arrive at them from first principles, by the following considerations. Let us take the first equation (*a*) as an example.

The chromium in potassium dichromate is in the state of CrO_3, and when reduced forms a chromic salt, *i.e.* it is reduced to the state Cr_2O_3. Hence $2CrO_3 \rightarrow Cr_2O_3 + 3O$, or two molecules of CrO_3 (*i. e.* one molecule of $K_2Cr_2O_7$, which may be regarded here as $K_2O, 2CrO_3$), will supply three atoms of oxygen. Also the K_2 wants SO_4 to form K_2SO_4, the $2Cr$ wants $3SO_4$ to form $Cr_2(SO_4)_3$, therefore $4H_2SO_4$ will be required. The fundamental equation therefore is—

(*a*) $K_2Cr_2O_7 + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$

A consideration of what is to be oxidised will show us how far these three oxygen atoms will go. In the present instance $2FeSO_4$ is going into $Fe_2(SO_4)_3$, or $2FeO \rightarrow Fe_2O_3$, *i.e.* one atom of oxygen will oxidise two molecules of a ferrous salt to the corresponding ferric salt. The three available atoms supplied by $K_2Cr_2O_7$ will therefore oxidise six molecules of ferrous sulphate to ferric sulphate, and also note that half as much SO_4 again is required as the ferrous salt already contains, thus—

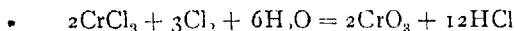
(*b*) $6FeSO_4 + 3H_2SO_4 + 3O \rightarrow 3Fe_2(SO_4)_3 + 3H_2O$

Adding equations (*a*) and (*b*) together, we have—

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

which is the required equation.

The other equations should be deduced in a similar way, *after performing the experiments and seeing what is produced.*

Problem 8.—*Oxidation of chromic salts in acid solution.*

(*a*) In the first case, no oxidation is noticed. *If* any took place it would obviously go thus—

$$2CrCl_3 + 3Cl_2 + 6H_2O = 2CrO_3 + 12HCl$$

But we saw in Problem 6 that hydrochloric acid will *reduce* chromic anhydride, CrO_3. Hence the above action is prevented by the presence of free acid. It will be found that the sulphate also will not be oxidised to chromic acid. But the oxidation is enabled to go if the free hydrochloric acid is replaced, as fast as it is formed, by acetic acid. This can be done by having plenty of sodium acetate present. Note that the chromic salt is now oxidised to the state of chromic acid, and that the solution reacts strongly acid. This will be due to free acetic acid, since the other acids liable to be formed (hydrochloric and chromic) will turn

out acetic acid from acetates. Test the solution for a chromate in the usual way (but remember that a chloride or a sulphate, or both, are also present, and therefore it is no use adding lead acetate straight away). The equation may be derived thus :—

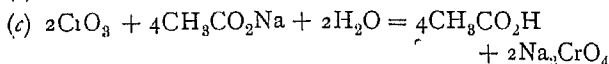
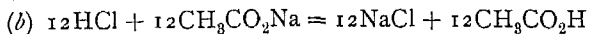
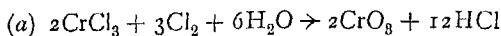
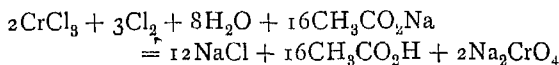
$2CrCl_3$ requires three oxygen atoms to oxidise it to chromic acid, thus—

(*a*) $2CrCl_3 + 3Cl_2 + 6H_2O \rightarrow 2CrO_3 + 12HCl$

(*b*) $12HCl + 12CH_3CO_2Na = 12NaCl + 12CH_3CO_2H$

(*c*) $2CrO_3 + 4CH_3CO_2Na + 2H_2O = 4CH_3CO_2H + 2Na_2CrO_4$

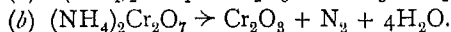
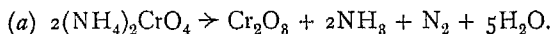
Adding up, we have—

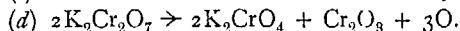
$$2CrCl_3 + 3Cl_2 + 8H_2O + 16CH_3CO_2Na = 12NaCl + 16CH_3CO_2H + 2Na_2CrO_4$$

The $12HCl$ and the $2CrO_3$ appear on each side of the total equation and therefore cancel out.

Problem 9.—Action of heat on chromates.

The reactions will be found to be as follows—

(*a*) $2(NH_4)_2CrO_4 \rightarrow Cr_2O_3 + 2NH_3 + N_2 + 5H_2O$.

(*b*) $(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O$.

(*c*) Potassium chromate is not reduced by heating alone.

(*d*) $2K_2Cr_2O_7 \rightarrow 2K_2CrO_4 + Cr_2O_3 + 3O$.

Confirm by heating strongly. Extract the residue with water. Test with litmus, and with acetic acid and lead acetate. Show that no bichromate is present. Show that during heating oxygen is evolved, also that chromic oxide is left.

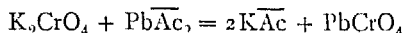
N.B.—Potassium dichromate, when gently heated, simply melts without decomposition.

(*e*) $2Hg_2CrO_4 = Cr_2O_3 + 4Hg + 5O$. Hence a good method for determining chromates. See also under Mercury.

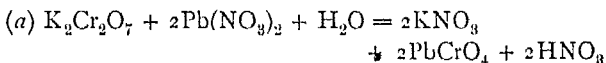
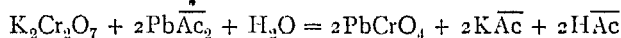
Problem 10.—*On the precipitation of the* CrO_4 *ion by lead.*

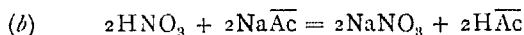
Lead chromate will be found to be soluble in dilute mineral acids, but insoluble in acetic acid.

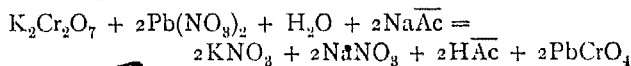
The action of lead acetate or nitrate on potassium chromate is to form lead chromate (insoluble) and potassium acetate or nitrate.

$$K_2CrO_4 + Pb\overline{Ac}_2 = 2K\overline{Ac} + PbCrO_4$$

Similarly with $Pb(NO_3)_2$. The CrO_4 is completely precipitated. But potassium dichromate, like any other acid salt, leaves the solution acid, thus—

$$K_2Cr_2O_7 + 2Pb\overline{Ac}_2 + H_2O = 2PbCrO_4 + 2K\overline{Ac} + 2H\overline{Ac}$$

$$(a)\ K_2Cr_2O_7 + 2Pb(NO_3)_2 + H_2O = 2KNO_3 + 2PbCrO_4 + 2HNO_3$$

In the former case, lead chromate being insoluble in acetic acid, all the CrO_4 will be precipitated. In the second case, however, since lead chromate is soluble in dilute nitric, some of the CrO_4 will remain in solution as free chromic acid, and will *not* be precipitated even by excess of lead nitrate. If, however, the nitric acid be replaced by acetic (by adding sodium acetate in excess), the CrO_4 will then be precipitated completely.

$$(b)\qquad 2HNO_3 + 2Na\overline{Ac} = 2NaNO_3 + 2H\overline{Ac}$$

Adding the two equations (a) and (b) together, we get—

$$K_2Cr_2O_7 + 2Pb(NO_3)_2 + H_2O + 2Na\overline{Ac} = 2KNO_3 + 2NaNO_3 + 2H\overline{Ac} + 2PbCrO_4$$

The action of barium chloride on potassium chromate and dichromate is absolutely similar.

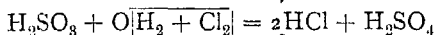
CHLORINE (p. 75).

Problem 1.—*The equivalent of chlorine.*

Sufficient details are given with the problem.

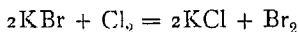
Problem 2.—Action of chlorine on sulphurous acid.

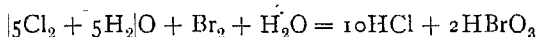
The chlorine oxidises the sulphurous acid to sulphuric, being itself reduced to hydrochloric acid. Thus—

$$H_2SO_3 + O|H_2 + Cl_2| = 2HCl + H_2SO_4$$

both of which may be found in the filtrate in the usual way, and separated if required by cautious distillation.

Problem 3.—Action of chlorine on a bromide.

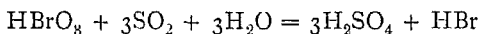
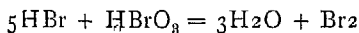
The first action of the chlorine is to turn out the bromine.

$$2KBr + Cl_2 = 2KCl + Br_2$$

The colour of the bromine, however, gradually disappears, and a solution having a strongly acid reaction and powerful oxidising properties is formed. On neutralising with potash and crystallising, a salt recognisable as potassium bromate ($KBrO_3$) will be found. The mother liquor will of course contain potassium chloride. Hence chlorine, in the presence of water, oxidises bromine to bromic acid. Since Br_2 requires $H_2O + 5O$ to form bromic acid, the reaction must be—

$$|5Cl_2 + 5H_2|O + Br_2 + H_2O = 10HCl + 2HBrO_3$$

The solution will be found to be capable of oxidising iodine to iodic acid, and sulphurous acid will be oxidised to sulphuric acid, with liberation of bromine, thus—

$$HBrO_3 + 3SO_2 + 3H_2O = 3H_2SO_4 + HBr$$

and then—

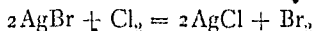
$$5HBr + HBrO_3 = 3H_2O + Br_2$$

(See also under Iodine, and under $\frac{N}{10}$ Thiosulphate, Problem 14.)

Problem 4.—Action of chlorine on an iodide.

The action will be found exactly similar to that on a bromide (Problem 3).

Problem 5.—Action of chlorine on silver bromide.

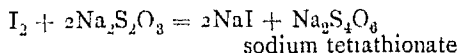
Silver chloride is formed thus—

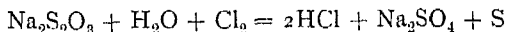
$$2AgBr + Cl_2 = 2AgCl + Br_2$$

A definite decrease in weight will thus take place, the ratio of the initial to the final weight being obviously AgBr : AgCl or 188 : 143·5. Care should be taken not to melt the substance in the boat, or particles of the bromide may get enclosed in the molten mass and escape the action of the chlorine. On heating in hydrogen the silver chloride is reduced to silver. The same difficulty occurs here, viz. danger of melting; otherwise the method is a good one for the determination of the equivalent of chlorine.

Problem 7.—Action of chlorine on a thiosulphate.

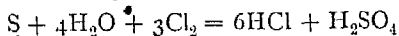
The action of chlorine on sodium thiosulphate is quite different from that of iodine.

The action of iodine is given under $\frac{N}{10}$ Thiosulphate estimations (p. 102), as follows—

$$I_2 + 2Na_2S_2O_3 = 2NaI + \underset{\text{sodium tetrathionate}}{Na_2S_4O_6}$$

Chlorine, however, oxidises the thiosulphate to sulphuric acid, with separation of sulphur, thus—

$$Na_2S_2O_3 + H_2O + Cl_2 = 2HCl + Na_2SO_4 + S$$

Strictly speaking, this is hardly an oxidation, for the thiosulphate is as fully oxidised as is the sulphate. It is rather a question of the replacement of sulphur by oxygen.

It is true that excess of the halogen will slowly oxidise this finely divided sulphur to sulphuric acid, thus—

$$S + 4H_2O + 3Cl_2 = 6HCl + H_2SO_4$$

The action of bromine on thiosulphate is similar to that of chlorine.

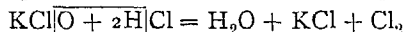
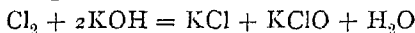
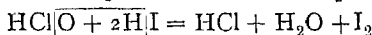
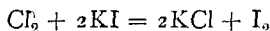
Problem 8.—Oxidising powers of chlorine and hypochlorites.

The oxidising power may be found by its action on KI, with subsequent titration of the liberated iodine. [See under Thiosulphate estimations.] After mixing the chlorine water and potash run into excess of potassium iodide, and acidify with dilute hydrochloric acid. Again titrate the liberated iodine.

The oxidising power will be the same before and after the addition of potash. This shows us that the hypochlorite formed has the same oxidising power as the chlorine that goes to form it.

$$Cl_2 + 2KOH = KCl + KClO + H_2O$$
$$KCl\boxed{O + 2H}Cl = H_2O + KCl + Cl_2$$

also

$$Cl_2 + 2KI = 2KCl + I_2$$
$$HCl\boxed{O + 2H}I = HCl + H_2O + I_2$$

Similarly a known volume of chlorine water will perform precisely the same amount of *any* oxidation as if it were neutralised with its equivalent of potash. Examples: the oxidation of ferrous salts to ferric, stannous chloride to stannic, etc.

BROMINE (p. 77).

Problem 1.—The equivalent of bromine.

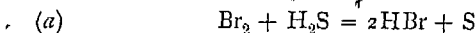
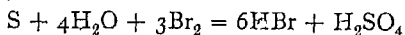
Sufficient details are given with the problem.

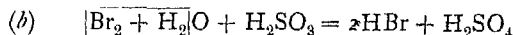
Problem 2.—Oxidising actions of bromine.

The actions which take place are as follows:—

(*a*) $Br_2 + H_2S = 2HBr + S$

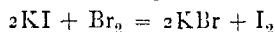
and gradually

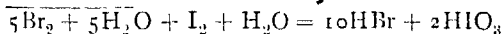
$$S + 4H_2O + 3Br_2 = 6HBr + H_2SO_4$$

Identify all these products in the resulting solution.

(*b*) $\boxed{Br_2 + H_2}O + H_2SO_3 = 2HBr + H_2SO_4$

Identify the products in the usual way Compare similar actions of chlorine.

Problem 3.—Action of bromine on an iodide.

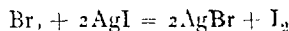
The first reaction that takes place is as follows—

$$2KI + Br_2 = 2KBr + I_2$$

The iodine liberated by the bromine dissolves in the chloroform or carbon disulphide added, forming a violet solution which is a very delicate test for an iodide. On adding excess of bromine water, the violet colour is discharged, and finally replaced by the brown colour of the excess of bromine itself, which also dissolves in the carbon disulphide. This is due to the oxidation of the iodine to iodic acid by the bromine, thus—

$$\overline{5Br_2 + 5H_2O} + I_2 + H_2O = 10HBr + 2HIO_3$$

Confirm the presence of these acids in the solution. (*Cf.* Problem 3 under Chlorine.)

Problem 4.—Action of bromine on silver iodide.

The action will be found to be as follows—

$$Br_2 + 2AgI = 2AgBr + I_2$$

The loss of weight can be determined, and will be proportional to the difference between AgI and AgBr, or, in other words, the ratio of the weight of iodide taken to that of bromide left will be the same as the ratio of AgI : AgBr, *i.e.* of 235 : 188.

Problem 5.—Percentage composition of a mixture of chloride, bromide, and iodide of silver.

Convert all the silver iodide into silver bromide by heating GENTLY a weighed portion of the mixture in a stream of bromine vapour (see Fig. 9). The loss of weight gives the percentage of silver iodide in the mixture.

Now convert the silver bromide into silver chloride by GENTLY heating in a stream of chlorine. The loss of weight will be a measure of the amount of silver bromide in the mixture of chloride and bromide. Of this, a known amount of bromide has come from the known amount of iodide; and hence the weight of silver bromide in the original mixture is found. The difference between the weights of bromide and iodide and the weight of mixture taken is the weight of the chloride.

Example.—W grams of the mixture are taken and heated in bromine. A loss of weight $= x$ occurs.

If AgI is turned into AgBr, for every 235 grams of iodide
235 188
present there will be a loss of weight of 47. Hence a loss x means that $\frac{x}{47} \times 235$ grams of silver iodide were present in W grams of the mixture.

Moreover, this weight of silver iodide, under the action of bromine, gives rise to the formation of $\frac{x \times 235}{47} \times \frac{AgBr}{AgI}$ grams of silver bromide, or $\frac{x \times 188}{47}$ grams of AgBr in W grams of the mixture.

Now heat this residue in chlorine. A further loss of weight, $= y$, occurs, owing to AgBr forming AgCl. Hence
188 143·5
a loss of weight of 44·5 means 188 grams of silver bromide are present.

$\therefore$ a loss of weight of $y = \frac{y \times 188}{44{\cdot}5}$ grams of silver bromide present.

Of this, $\frac{x \times 188}{47}$ grams resulted from the conversion of odide into bromide.

∴ weight of AgBr present in W grams of the original mixture $= \frac{y \times 188}{44 \cdot 5} - \frac{x \times 188}{47}$.

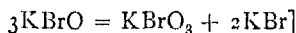
The weight of chloride follows at once.

Problem 6.—Preparation of potassium bromate and bromide.

In hot solution the action of bromine on potash is—

$$3Br_2 + 6KOH = 5KBr + KBrO_3 + 3H_2O$$

[This is the result, remember, of the autoxidation of the hypobromite first formed.

$$3KBrO = KBrO_3 + 2KBr]$$

Hence to a solution of potash, not too dilute, add very cautiously, in the draught cupboard, from a dropping funnel, slightly more than the calculated amount of bromine (to allow for loss by volatilisation). The mixture gets hot, and the conversion of hypobromite into bromate is complete. Finally dilute with hot water, filter if necessary, and evaporate down till a test drop readily crystallises. Stand aside for the bromate to crystallise out, and recrystallise the crop from a little hot water.

The bromide is got from the residue by evaporating dry, mixing with a little powdered charcoal, and igniting. When cold, extract with hot water and crystallise in the usual way. The charcoal is to effect the complete reduction of any bromate left, as the temperature of decomposition is higher than that of potassium chlorate.

Problem 8.—Action of bromine on a thiosulphate.

The action is precisely similar to that of chlorine (*q.v.* Problem 7, under Chlorine).

IODINE (p. 78).

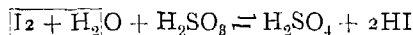
Problem 1.—The equivalent of iodine.

Sufficient details are given with the problem.

Problem 2.—Some oxidising actions of iodine.

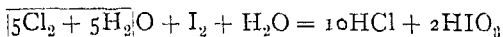
The action of iodine on sulphurous acid and on hydrogen sulphide is similar to the action of bromine and chlorine, with the exceptions that—

(*a*) In the case of sulphurous acid, the oxidation to sulphuric is only complete in the presence of excess of iodine, or, in other words, the reaction

$$I_2 + H_2O + H_2SO_3 \rightleftharpoons H_2SO_4 + 2HI$$

is reversible. [*Cf.* Problem 3, under $\frac{N}{10}$ Thiosulphate.]

(*b*) In the case of hydrogen sulphide, the reaction $H_2S + I_2 = 2HI + S$ takes place only in the presence of water, and ceases when the solution reaches a specific gravity of 1·56. **Naumann** has shown that this is because the combination of hydrogen and iodine takes place with absorption of heat, and the heat of solution of the resulting hydriodic acid supplies the necessary heat to carry on the reaction. After a time, however, the solution gets sufficiently strong in hydriodic acid to prevent the solution of a further quantity giving out enough heat to enable the reaction to proceed.

(*c*) The action of chlorine on iodine is exactly similar to the action of chlorine on bromine and of bromine on iodine (*q. v.*), viz.—

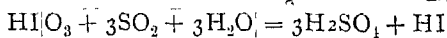
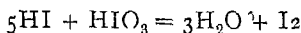
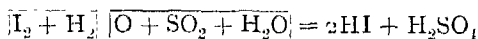
$$5Cl_2 + 5H_2O + I_2 + H_2O = 10HCl + 2HIO_3$$

Sulphur dioxide will liberate iodine from iodic acid; hence the use of sulphurous acid in testing for an iodate.

$$HIO_3 + 3SO_2 + 3H_2O = 3H_2SO_4 + HI$$

and then

$$5HI + HIO_3 = 3H_2O + I_2$$

Note also that—

$$I_2 + H_2O + SO_2 + H_2O = 2HI + H_2SO_4$$

and therefore the appearance of the iodine is delayed, especially in dilute solution, until all the sulphur dioxide added has been used up. [Hence avoid excess.] Try this, using some starch solution as indicator. Often nearly a minute may elapse between the addition of the sulphurous acid to the dilute iodate and the *sudden* appearance of the blue colour.

Note that this problem, and Nos. 3, 4 and 5 under Bromine, and 3 under Chlorine, show us that the affinity of chlorine for hydrogen is greater than that of bromine, which again is greater than that of iodine. Otherwise expressed, chlorine will displace both bromine and iodine from bromides and iodides, and bromine will displace iodine from iodides.

With their oxygen acids, however, the reverse is true. Iodine will displace both chlorine and bromine from chlorates and bromates, and bromine will displace chlorine from chlorates.

Problem 3.—*Action of iodine on a chlorate.*

Chlorine is given off, and potassium iodate, KIO_3, is left, thus—

$$2KClO_3 + I_2 = 2KIO_3 + Cl_2$$

Test for the iodate by adding sulphurous acid solution and watching for the liberation of iodine, as in Problem 2 above.

Problem 4.—*Oxidation of iodine by nitric acid.*

Strong nitric acid oxidises iodine to iodic acid, which is a white crystalline substance. The action of gentle heat is to dehydrate these crystals and give iodine pentoxide, I_2O_5. This, on further heating, liberates oxygen, and iodine is left on the cool parts of the tube. Iodic acid, HIO_3, is a fairly powerful oxidising agent. Try some of its reactions, *e.g.* on ferrous salts, potassium iodide, etc.

MANGANESE (p. 80).

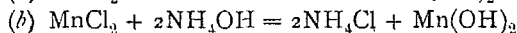
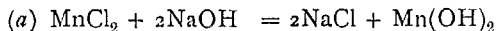
Problem 1.—*To find the equivalent.*

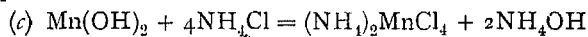
Sufficient details are given with the problem.

Problems 2 *and* 3.—*Some properties of manganous hydroxide.*

Both soda and ammonia precipitate white manganese hydroxide, $Mn(OH)_2$, from solutions of manganous salts.

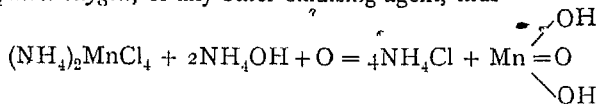
(*a*) $MnCl_2 + 2NaOH = 2NaCl + Mn(OH)_2$

(*b*) $MnCl_2 + 2NH_4OH = 2NH_4Cl + Mn(OH)_2$

When ammonia is used, however, the ammonium salt formed dissolves the hydroxide according to the following equation—

(*c*) $Mn(OH)_2 + 4NH_4Cl = (NH_4)_2MnCl_4 + 2NH_4OH$

and the manganese in this complex salt is not precipitated by ammonia. It will be noted, moreover, that the amount of ammonium chloride formed according to (*b*) is sufficient to dissolve one half of the hydroxide precipitated, to form this complex salt. Thus, in the absence of ammonium salts, ammonia precipitates one half only of the manganese, thus—

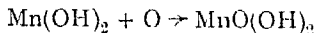
$$2MnCl_2 + 2NH_4OH = MN(OH)_2 + (NH_4)_2MnCl_4$$

If ammonium chloride be added first, and then the ammonia, *all* the manganese will be dissolved to form this complex salt. BUT this salt is readily acted on by *atmospheric oxygen*, or any other oxidising agent, thus—

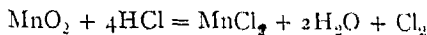
$$(NH_4)_2MnCl_4 + 2NH_4OH + O = 4NH_4Cl + Mn\begin{cases}OH\\=O\\OH\end{cases}$$

$Mn\begin{cases}OH\\=O\\OH\end{cases}$ is obviously hydrated manganese dioxide, and

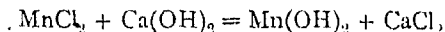
is quite insoluble in ammonium salts, and therefore after standing for a time we get a brown precipitate. This explains the presence of manganese in Group III A precipitate in qualitative analysis, if that element is present in the solution.

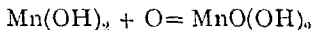
In any case, if the precipitate of manganous oxide is obtained, any oxidising agent, including the oxygen of the air, will oxidise it—

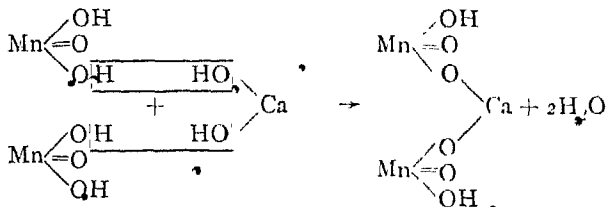
$$Mn(OH)_2 + O \rightarrow MnO(OH)_2$$

so that the white precipitate gradually turns brown.

This ready oxidisability of manganous hydroxide is the basis of the **Weldon** process for the recovery of manganese dioxide for the manufacture of chlorine. Thus—

$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$

The acid liquor containing the manganous salt is allowed to settle, and the clear solution drawn off into a tank, where it is treated with excess of milk of lime.

$$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2$$

This liquor is then heated by steam, and air blown rapidly in. Then—

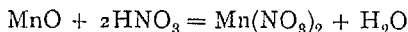
$$Mn(OH)_2 + O = MnO(OH)_2$$

which is hydrated MnO_2. Being an acid, it combines with the excess of slaked lime, thus—

$$\mathrm{Mn}\begin{cases}\mathrm{OH}\\ =\mathrm{O}\\ \mathrm{OH}\end{cases} + \begin{matrix}\mathrm{HO}\\ \mathrm{HO}\end{matrix}\!\!>\!\mathrm{Ca} + \mathrm{Mn}\begin{cases}\mathrm{OH}\\ =\mathrm{O}\\ \mathrm{OH}\end{cases} \rightarrow \begin{matrix}\mathrm{Mn}\begin{cases}\mathrm{OH}\\ =\mathrm{O}\\ \mathrm{O}\end{cases}\\ \mathrm{Mn}\begin{cases}\mathrm{O}\\ =\mathrm{O}\\ \mathrm{OH}\end{cases}\end{matrix}\!\!>\!\mathrm{Ca} + 2H_2O$$

This substance, $CaH_2(MnO_3)_2$ is obviously calcium bi-mangan*ite* (*cf.* $CaH_2(CO_3)_2$, calcium bicarbonate). It is a

dark brown, insoluble substance. It is allowed to settle, and the clear liquor is run off from above it. The "mud" is then put back into the chlorine still, and treated with hydrochloric acid again for the preparation of chlorine. Note, however, that more hydrochloric acid is now required, as calcium chloride has to be formed as well as manganous chloride. The "mud," however, acts with hydrochloric acid much more readily than does native pyrolusite.

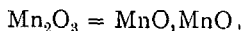
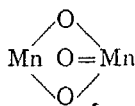
Problem 4.—Distinction between the oxides of manganese.

The action of hot dilute nitric acid on the oxides Mn_2O_3 and Mn_3O_4 is to dissolve part of the manganese to form manganous nitrate, and the remainder is left in the form of hydrated manganese dioxide (evolves chlorine with hot strong hydrochloric acid). Since the oxide MnO (if obtainable) would obviously form manganese nitrate and water with nitric acid, thus—

$$MnO + 2HNO_3 = Mn(NO_3)_2 + H_2O$$

it would seem as though the other two oxides were compounds of MnO and MnO_2, or, in other words, were the manganese salts of manganous acid, thus—

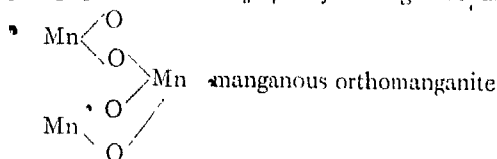
$$Mn_2O_3 = MnO,MnO_2$$

or—

```
      O
    /   \
Mn   O=Mn
    \   /
      O
```

```
                                  HO\
i. e. the manganous salt of        O=Mn
                                  HO/   (manganous acid).
```

Mn_3O_4 is $2MnO,MnO_2$, *i. e.* it is basic manganous manganite, or, more correctly, the manganese salt of ORTHO-

manganous acid, *i.e.* the fully hydrated $Mn(OH)_4$ [*i.e.* $MnO_2, 2H_2O$]. Hence Mn_3O_4 may be regarded as—

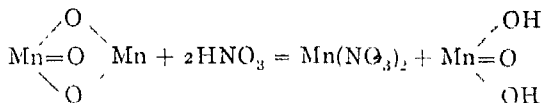
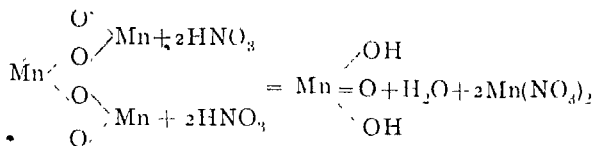
$$\begin{array}{l} Mn\langle{}^{O}_{O}\rangle Mn \quad \text{manganous orthomanganite} \\ Mn\langle{}^{O}_{O}\rangle \end{array}$$

The previous oxide, Mn_2O_3, is thus manganous meta manganite. (*Cf.* carbonic and silicic acids.)

The reaction with nitric acid of these two oxides, according to the above scheme, will therefore be—

For Mn_2O_3—

$$Mn{\equiv}(O)_3{\equiv}Mn + 2HNO_3 = Mn(NO_3)_2 + Mn{=}O(OH)_2$$

For Mn_3O_4—

$$Mn\langle{}^{O_2\rangle Mn + 2HNO_3}_{O_2\rangle Mn + 2HNO_3} = Mn{=}O(OH)_2 + H_2O + 2Mn(NO_3)_2$$

It is obvious that the above ideas can easily be tested. All that is necessary is to determine the ratio of the manganese dissolved to the manganese left, after treatment with nitric acid. In the case of Mn_2O_3, the two quantities of manganese will be equal, and in the case of Mn_3O_4, as 2 : 1. The actual experimental part is left to the student's own ingenuity, with the help of a book on Quantitative Analysis.

The action of hydrochloric acid on these three oxides will be, of course, to form manganous chloride and chlorine, since the MnO_2 they all contain is soluble in hot strong

hydrochloric acid. Hence the distinction between manganese dioxide and the other two oxides with nitric acid is necessary. (See also under Lead, p. 155.)

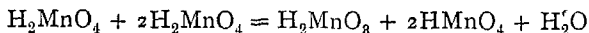
Problem 5a.—Manganic acid and manganates.

If we attempt to prepare free manganic acid by acidifying a manganate, we obtain permanganate acid and a precipitate of hydrated MnO_2. This shows us that manganic acid will oxidise part of itself to permanganic acid, the oxidising portion becoming reduced to MnO_2 in the process. The best way to get at the equation is to consider simply the anhydrides, and we shall see at once how much oxgyen is given up and required. Thus—

$MnO_3 \rightarrow MnO_2 + O$, or a molecule of MnO_3 supplies an atom of oxygen.

$2MnO_3$ wants an atom of O to form Mn_2O_7 (permanganic anhydride), and is therefore oxidised by one molecule of MnO_3 as above.

Hence $MnO_3 + 2MnO_3 = MnO_2 + Mn_2O_7$, or, adding water to each anhydride (since we have actually to deal with the hydrated form)—

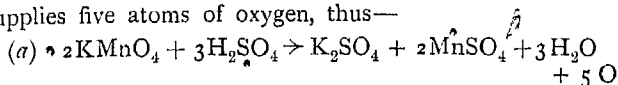
$$H_2MnO_4 + 2H_2MnO_4 = H_2MnO_3 + 2HMnO_4 + H_2O$$

Nitric acid will be found to act similarly to carbonic. If hydrochloric be used, the $MnO(OH)_2$ may be dissolved, with evolution of chlorine, and consequently will be missed.

Query.—What other examples have you come across of substances oxidising themselves? (See Hypochlorites, Sulphites, etc.)

Problem 5b.—Oxidations by permanganates.

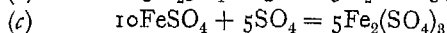
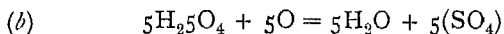
(i) In acid solution it will be found that in every case the permanganate is reduced to a manganous salt, *i.e.* $Mn_2O_7 \rightarrow 2MnO + 5O$.

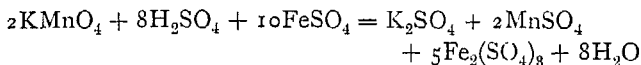
Hence permanganic anhydride, Mn_2O_7 (*i.e.* $2KMnO_4$), supplies five atoms of oxygen, thus—

(*a*) $2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$

The student should be able to make out the equations for the oxidising action of these five oxygen atoms on the various reducing agents tried. [Compare potassium dichromate.] *E.g.* $2FeO \rightarrow Fe_2O_3$ with one atom of oxygen, hence five atoms will oxidise $10FeO$.

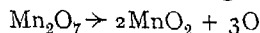
If $10FeSO_4 \rightarrow 5Fe_2(SO_4)_3$, five more (SO_4)'s will be required, which are supplied thus—

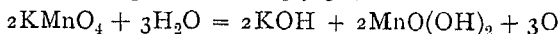
(*b*) $5H_2SO_4 + 5O = 5H_2O + 5(SO_4)$

(*c*) $10FeSO_4 + 5SO_4 = 5Fe_2(SO_4)_3$

Adding (*a*), (*b*), and (*c*) together, and cancelling what comes on both sides, we have—

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 = K_2SO_4 + 2MnSO_4 + 5Fe_2(SO_4)_3 + 8H_2O$$

Similarly deduce the action on stannous chloride, hydrogen peroxide, etc.

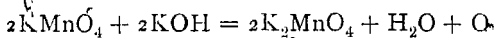
(ii) In neutral solution, we shall find in every case that the permanganate is only reduced to manganese dioxide, a hydrated precipitate of this oxide being left every time, or—

$$Mn_2O_7 \rightarrow 2MnO_2 + 3O$$

Hence $2KMnO_4$ can only supply $3O$, which it does thus—

$$2KMnO_4 + 3H_2O = 2KOH + 2MnO(OH)_2 + 3O$$

Make out equations as in (ii), and notice that the solution goes *alkaline* every time. (*Cf.* Problem 5.)

(iii) In alkaline solution, the permanganate is *sometimes* only reduced as far as the manganate, shown by the purple solution turning green. This is not always the case, however, the action often going as in (ii), and the permanganate being reduced to manganese dioxide (always hydrated).

The slight reduction to manganate is shown by the oxidation of a citrate. Thus—

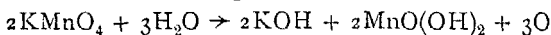
$$2KMnO_4 + 2KOH = 2K_2MnO_4 + H_2O + O$$

and a green solution results.

The $H_2O + O$ sometimes acts as $2OH$. Hence alkaline permanganate is a very gentle oxidising agent.

Problem 6.—*Action of a permanganate on potassium iodide.*

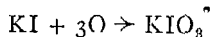
Note the following points:—

(i) The manganese has been reduced from permanganate to manganous acid (MnO_2) or, according to Problem 4*b*—

$$2KMnO_4 + 3H_2O \rightarrow 2KOH + 2MnO(OH)_2 + 3O$$

That the solution is now strongly alkaline confirms this.

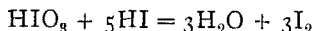
(ii) No free iodine is noted, hence the iodide has been oxidised *further* than merely to iodine, which is the first possible stage.

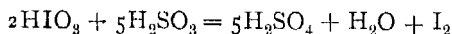
The $3O$ naturally suggests an iodate, and on testing the crystals obtained, we find this to be the case.

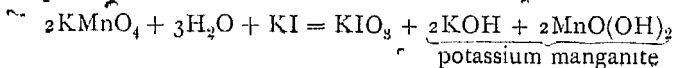
$$KI + 3O \rightarrow KIO_3$$

To test for an iodate—

(*a*) Heat the dry crystals: oxygen is evolved, and an iodide left.

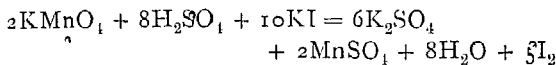
(*b*) Mix the solution with potassium iodide solution and acidify. Iodine is formed.

$$HIO_3 + 5HI = 3H_2O + 3I_2$$

(*c*) Treat the solution with sulphurous acid. Iodine set free.

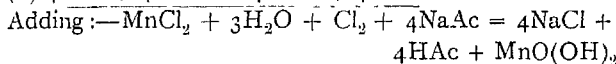
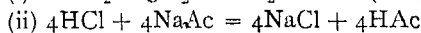
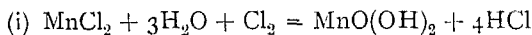
$$2HIO_3 + 5H_2SO_3 = 5H_2SO_4 + H_2O + I_2$$

Hence the complete action of neutral permanganate on potassium iodide is—

$$2KMnO_4 + 3H_2O + KI = KIO_3 + \underbrace{2KOH + 2MnO(OH)_2}_{\text{potassium manganite}}$$

The potash is neutralised with acetic acid before crystallising the iodate.

If the solution of the iodide is *acid*, permanganate simply liberates iodine in the usual way.

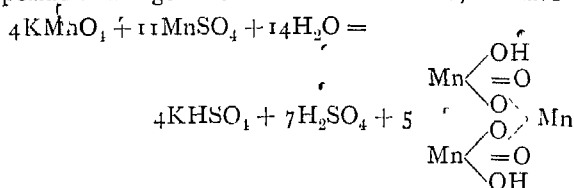
$$2KMnO_4 + 8H_2SO_4 + 10KI = 6K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$$

Problem 7.—Oxidation of manganous manganese.

We note that the manganese is oxidised completely to the state of MnO_2, as the black precipitate formed answers to the tests for this oxide. Also that the solution has become acid. Since sodium acetate is present, there must be free acetic acid present. Now chlorine will not oxidise $MnCl_2$ in neutral solution, because free HCl would be at once produced, which would stop the action. (Compare Chromium, Problem 7.) The acetate replaces this HCl by acetic acid. Hence equation is obviously :—

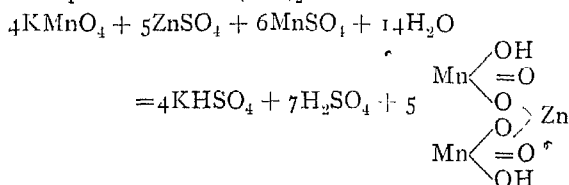
(i) $MnCl_2 + 3H_2O + Cl_2 = MnO(OH)_2 + 4HCl$
(ii) $4HCl + 4NaAc = 4NaCl + 4HAc$
Adding :—$MnCl_2 + 3H_2O + Cl_2 + 4NaAc = 4NaCl + 4HAc + MnO(OH)_2$

Problem 8.—Further investigation of the oxidation of manganous salts in acid solution.

In this case we get a brown precipitate, and the solution reacts acid. If the precipitate be carefully washed, hot dilute nitric acid will be found to dissolve a certain amount of manganese out of it, leaving the hydrated dioxide $MnO(OH)_2$. (Proof?) Hence a manganese manganite (probably Mn_2O_3,H_2O) has been formed, and the action has *not* gone to the end [*i. e.* forming the dioxide and nothing else]. A definite equation hardly represents what actually goes on here, because the composition of the precipitate varies somewhat with different conditions.

Assuming that the manganous manganite formed has a composition analogous to that of Weldon mud, we have—

$$4KMnO_4 + 11MnSO_4 + 14H_2O = 4KHSO_4 + 7H_2SO_4 + 5 \begin{matrix} Mn \left\langle \begin{matrix} OH \\ =O \\ O \end{matrix} \right. \\ \rangle Mn \\ Mn \left\langle \begin{matrix} O \\ =O \\ OH \end{matrix} \right. \end{matrix}$$

Deduce this by stages in the usual way.

Volhard has shown that in the presence of zinc salts, zinc manganite is precipitated, so that all the manganese is present in the tetravalent form. Hence in the second case, if the liquid be approximately neutralised after the addition of the permanganate, the precipitate will be found to consist of zinc manganite, as hot dilute nitric acid dissolves zinc out of it, but no manganese. As the manganese is now all present as $MnO(OH)_2$—

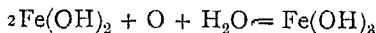
$$4KMnO_4 + 5ZnSO_4 + 6MnSO_4 + 14H_2O = 4KHSO_4 + 7H_2SO_4 + 5 \begin{matrix} Mn \left\langle \begin{matrix} OH \\ =O \\ O \end{matrix} \right. \\ \rangle Zn \\ Mn \left\langle \begin{matrix} O \\ =O \\ OH \end{matrix} \right. \end{matrix}$$

IRON (p. 85).

Problem 1.—*The equivalents of iron.*

Sufficient details have been given with the problem.

Problem 2.—*Distinctions between ferrous and ferric salts.*

Caustic soda on ferrous salts gives a precipitate of ferrous hydroxide, which is white when *absolutely* ferrous, but it rapidly absorbs oxygen, turning green, black, and finally brown.

$$2Fe(OH)_2 + O + H_2O = Fe(OH)_3$$

Ammonia precipitates one half of the iron as ferrous hydroxide, the other half going into solution as $(NH_4)_2FeCl_4$ exactly as $Mn(OH)_2$ does. [See under Manganese, Problem 21] It is oxidised similarly with greater readiness. The action of both soda and ammonia on ferric salts is to precipitate completely ferric hydroxide, $Fe(OH)_3$.

Potassium ferrocyanide.—From ferrous salts precipitates white ferrous ferrocyanide, which rapidly absorbs oxygen and goes into ferric ferrocyanide, which is deep blue. Hence we generally get a *light* blue precipitate.

From ferric salts, dark blue ferric ferrocyanide is precipitated (Prussian blue).

Potassium ferricyanide.—From ferrous salts precipitates dark blue ferrous ferricyanide (Turnbull's blue).

With ferric salts gives a brownish coloration of ferric ferricyanide. With this brown solution, reducing agents give a blue precipitate of ferrous ferricyanide.

Potassium sulphocyanate gives nothing with absolutely *ferrous* solutions, but with ferric gives a blood-red coloration due to ferric sulphocyanate. With ferrous salts, though, one practically always gets this coloration owing to slight oxidation.

The best distinction between ferrous and ferric salts is potassium ferricyanide.

The best way to test for ferrous and ferric salts when mixed is to try the action of—

(*a*) NaOH, and note colour of precipitate. If purely ferrous it will be a dirty green. If ferric salts are present as well, it will be black.

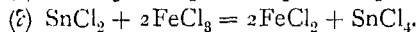
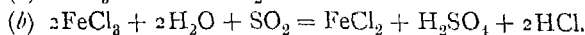
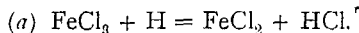
(*b*) Add potassium ferricyanide. A blue precipitate indicates a ferrous salt. Filter. A brown filtrate indicates ferric.

Problem 3.—Reduction of ferric salts.

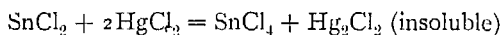
All these reducing agents will be found to reduce ferric salts to ferrous.

(*a*) $FeCl_3 + H = FeCl_2 + HCl.$

(*b*) $2FeCl_3 + 2H_2O + SO_2 = FeCl_2 + H_2SO_4 + 2HCl.$

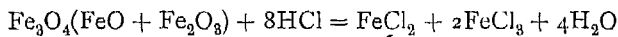
(*c*) $SnCl_2 + 2FeCl_3 = 2FeCl_2 + SnCl_4.$

All these oxidising agents will oxidise ferrous iron to ferric. The equations should be sufficiently obvious, and most of them have already been given.

The best way to reduce ferric iron to ferrous (or dichromate titration) is to add a *slight* excess of stannous chloride. The excess of stannous chloride is removed by adding mercuric chloride solution.

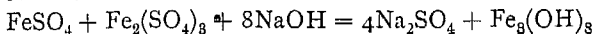
$$SnCl_2 + 2HgCl_2 = SnCl_4 + Hg_2Cl_2 \text{ (insoluble)}$$

If permanganate is being used, chlorides must not be present, so nascent hydrogen is used.

Problem 4.—Oxidation of ferrous hydroxide.

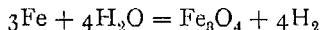
The results here have already been indicated under Problem 1. Note that a mixture of ferrous and ferric iron in the proportion 1 : 2 gives a *black* precipitate. In (*c*), note that on adding soda to this solution, we get the black precipitate indicated above. Moreover, on testing with ferricyanide, etc., both ferrous and ferric salts are found to be present. It looks therefore as if Fe_3O_4 contained both ferrous and ferric oxides. Its formula therefore must be FeO,Fe_2O_3, and the action with hydrochloric acid as follows—

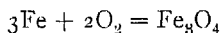
$$Fe_3O_4(FeO + Fe_2O_3) + 8HCl = FeCl_2 + 2FeCl_3 + 4H_2O$$

This can easily be shown to be the case by estimating the ratio between ferrous and ferric iron in the solution. For details see under Volumetric Analyses with potassium di-

chromate. If ferrous and ferric salts be mixed in the proportion of 1 : 2, and precipitated with caustic soda, we shall get the hydroxide of Fe_3O_4 (*i.e.* $Fe(OH)_2,2Fe(OH)_3$ or $Fe_3(OH)_8$), thus—

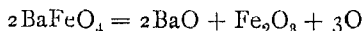
$$FeSO_4 + Fe_2(SO_4)_3 + 8NaOH = 4Na_2SO_4 + Fe_3(OH)_8$$

On igniting in a stream of carbon dioxide, or nitrogen, this hydroxide will be dehydrated, $Fe_3(OH)_8 = Fe_3O_4 + 4H_2O$.

The best way of preparing Fe_3O_4 is to heat iron in steam.

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2$$

or burn iron wire in oxygen.

$$3Fe + 2O_2 = Fe_3O_4$$

Problems 5 and 6.—Oxidation of ferric compounds.

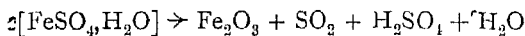
The purple solutions will in both cases contain potassium ferrate, K_2FeO_4, analogous to potassium manganate, K_2MnO_4. But the oxide FeO_3 corresponding has never been prepared. Even the ferrate solution is unstable, and is immediately reduced by reducing agents. Addition of barium chloride will precipitate insoluble barium ferrate, $BaFeO_4$. The action of heat on this will be—

$$2BaFeO_4 = 2BaO + Fe_2O_3 + 3O$$

Test for oxygen, and confirm by the obvious way of (*a*) testing the solution of the residue with litmus (for baryta), and (*b*) extracting with hot hydrochloric acid and testing for a ferric salt.

Problem 7.—Action of heat on ferrous sulphate crystals.

The first stage in the action of heat on $FeSO_4,7H_2O$ crystals is to drive off all the water of crystallisation except one molecule. A temperature of about 120° C. will do this. The remaining molecule cannot be driven off without total decomposition of the salt. Water, sulphur dioxide

and trioxide may all be identified in the evolved gases, and ferric oxide is left. This has evidently been oxidised at the expense of the sulphur trioxide which one would expect to get from a sulphate, and since $SO_3 \rightarrow SO_2 + O$ and $2FeO + O \rightarrow Fe_2O_3$, we can arrive at the equation—

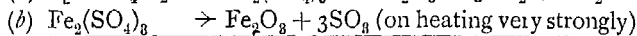
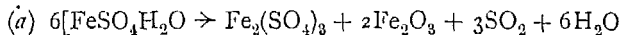
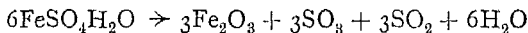
$$2[FeSO_4,H_2O] \rightarrow Fe_2O_3 + SO_2 + H_2SO_4 + H_2O$$

Really, however, the reaction is not quite so simple, for on extracting the half-decomposed mass with water, ferric sulphate will be found in it. Hence $FeSO_4$ is oxidised to $Fe_2(SO_4)_3$ as well as to Fe_2O_3 by the first portion of SO_3 given off.

The equation therefore becomes—

(*a*) $6[FeSO_4H_2O \rightarrow Fe_2(SO_4)_3 + 2Fe_2O_3 + 3SO_2 + 6H_2O$

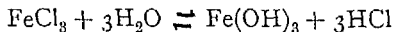
(*b*) $Fe_2(SO_4)_3 \rightarrow Fe_2O_3 + 3SO_3$ (on heating very strongly)

Adding, we get—

$$6FeSO_4H_2O \rightarrow 3Fe_2O_3 + 3SO_3 + 3SO_2 + 6H_2O$$

which is the same as the simplified equation given first.

Problem 8.—*The hydrolysis of ferric salts.*

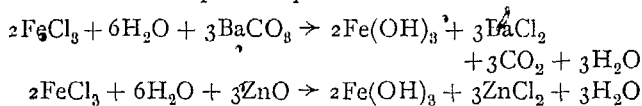
When a ferric salt is warmed in solution with an oxide, hydroxide, or carbonate of the divalent metals, such as the alkaline earths, magnesium, zinc, copper, etc., it will be found that the iron is completely precipitated after a time as ferric hydroxide. This is due to the fact that ferric salts are partly hydrolysed in aqueous solution, thus—

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

In presence of excess of water, the reaction goes to the right; in presence of excess of acid it goes to the left. [*N.B.*—This is best seen in the case of ferric acetate. Try this.]

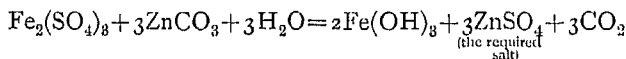
Also on removing the hydrochloric acid, the reaction naturally goes to the right. The acid can be removed

either by carbonates, oxides or hydroxides of the divalent metals. The completed equation therefore becomes—

$$2FeCl_3 + 6H_2O + 3BaCO_3 \rightarrow 2Fe(OH)_3 + 3BaCl_2 + 3CO_2 + 3H_2O$$

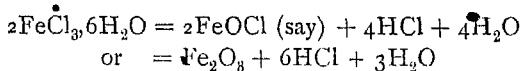
$$2FeCl_3 + 6H_2O + 3ZnO \rightarrow 2Fe(OH)_3 + 3ZnCl_2 + 3H_2O$$

Similarly for ferric sulphate and other ferric salts. This gives us a very useful method of freeing salts from iron, which is the most common impurity.

E.g. pure zinc sulphate is wanted from commercial zinc, in which the chief impurities are carbon, arsenic and iron. Dissolve it in dilute sulphuric acid. Carbon is left, arsenic goes off as arsine, and iron dissolves as ferrous sulphate. A little nitric acid is added and the whole rapidly crystallised. This oxidises ferrous salts to ferric, and the excess of nitric acid is got rid of. Dissolve up in water, and add a little of the oxide or carbonate of the metal whose salt you are preparing (zinc in this case). This carbonate is got by precipitating, say, one-twelfth of the liquor with sodium carbonate, filtering and washing the precipitated zinc carbonate, adding it to the main solution, and digesting hot for some time, till a test portion of the filtrate fails to give a test for iron.

$$Fe_2(SO_4)_3 + 3ZnCO_3 + 3H_2O = 2Fe(OH)_3 + \underset{\text{(the required salt)}}{3ZnSO_4} + 3CO_2$$

Problem 9.—Action of heat on ferric salts.

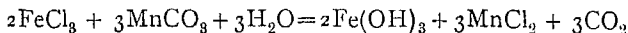
The solid substance [$FeCl_3,6H_2O$], on heating, will be found to evolve hydrochloric acid as well as water, and either ferric oxide will be left, or, at any rate, an insoluble basic choride.

$$2FeCl_3,6H_2O = 2FeOCl \text{ (say)} + 4HCl + 4H_2O$$
$$\text{or} \quad = Fe_2O_3 + 6HCl + 3H_2O$$

P 2

Hence if a salt of a divalent metal contains *large* amounts of iron as an impurity, evaporate to dryness and heat as strongly as a *sand-bath* allows. By this means the ferric salt (chloride or sulphate) will be largely decomposed into an insoluble basic salt, whereas the salt of the divalent metal will be stable under these conditions. Extract with water, filter, and get rid of the last traces of iron as above (Problem 8).

Problem 10.—*Manganous chloride from pyrolusite.*

The commercial article, dissolved in strong hydrochloric acid, will give us manganous choride ($MnCl_2$) and ferric chloride ($FeCl_3$). No ferrous salt will be present, owing to the free chlorine that has been coming off. Evaporate dry, and heat as indicated in Problem 9. Extract with water, filter, get rid of the last traces of iron by precipitating manganous carbonate from one-twelfth of the solution, and digesting it with the main portion till a filtered test shows absence of iron. Then filter and crystallise.

$$2FeCl_3 + 3MnCO_3 + 3H_2O = 2Fe(OH)_3 + 3MnCl_2 + 3CO_2$$

Problem 11.—*Purification of copper sulphate from ferrous sulphate.*

In this case, strongly heating is apt to decompose the copper sulphate somewhat, though not much. But by first oxidising the iron to ferric sulphate by nitric acid, and then *crystallising*, most of the iron is got rid of, as ferric sulphate is extremely soluble, and non-crystalline. The remaining traces are got rid of as in Problem 10.

Problem 12.

See Problem 8 for details.

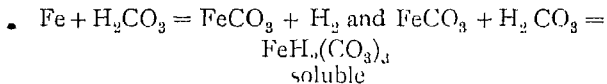
Problem 13.—*The rusting of iron.*

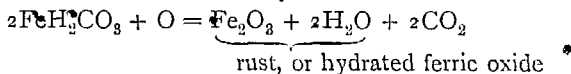
(*a*) It will be noticed in this problem that rusting may or may not take place, according to the care with which air has been excluded, and that small quantities of a gas *may* collect in the test-tube. If sufficient is collected, it may be shown to be hydrogen, though great difficulty will be experienced in getting enough.

Evidently, then, the iron dissolves in the tap-water somehow.

(*b*) Comparing the results of the next experiment * [which was published by Dr. Moody in the *School World*, Jan. 1907], we note that though the nails remain bright, the upper part of the solution is turbid, and plenty of rust settles on the piece of filter-paper. Putting these results together, and remembering that ferrous salts go into basic ferric salts with oxygen, we arrive at the following conclusions—

(i) The iron must dissolve to form ferrous hydrogen carbonate, as this is the only possible soluble ferrous compound under the condition. Probably therefore:—

$$Fe + H_2CO_3 = FeCO_3 + H_2 \text{ and } FeCO_3 + H_2CO_3 = \underset{\text{soluble}}{FeH_2(CO_3)_2}$$

(ii) This gets oxidised by atmospheric oxygen to ferric carbonate, which, however, cannot exist, and immediately breaks up into carbon dioxide and ferric oxide, thus—

$$2FeH_2CO_3 + O = \underbrace{Fe_2O_3 + 2H_2O}_{\text{rust, or hydrated ferric oxide}} + 2CO_2$$

The formation of hydrogen is the most difficult part of this problem to show. It has been done by very careful experiments, but the conditions necessary to get any

* See also *Proceedings of the Chemical Society*, March 28, 1907.

quantity are to have a strong solution of carbonic acid in absolutely air-free water, and rigidly exclude air. It has been proved that under these conditions the iron goes into solution,* but no rusting takes place.

Problem 14.—*On the rusting of "tin-plate" and the non-rusting of "galvanised" iron.*

The apparatus is set up as shown in figure.

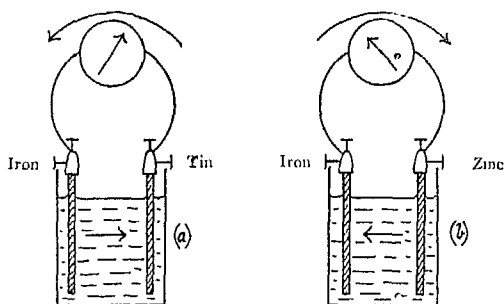



FIG. 20.

In the iron-tin cell, the current will be found (by comparing the deflection of the galvanometer with that produced by a current whose direction is known) to be flowing from tin to iron *outside* the cell, as indicated. This means that the iron is acting as the soluble metal, producing, of course, ferrous hydrogen carbonate, which is then being oxidised as in Problem 12 above. A copious deposit of rust will be noted if the circuit is left closed overnight.

In the iron-zinc cell, we see that the current goes from iron to zinc outside the cell, and therefore the zinc is the dissolving metal, whilst the iron is kept out of solution

* For latest work, see Lambert and Thomson, *Trans of the Chem Soc.*, 1910, p 2426.

by the direction of the current inside the cell, which will obviously deposit on the iron plate any chance Fe ions that get into the solution. No rusting whatever will be observed as long as the circuit is closed.

The application to tin-plate and galvanised iron is obvious.

NICKEL AND COBALT (p. 91).

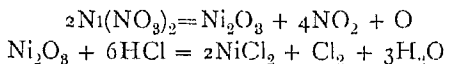
Problem 1.—The equivalents.

The usual "nitrate method" is not available, because by ignition of the nitrate it is very difficult to get an absolutely pure oxide.

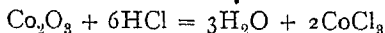
At low red heat Ni_2O_3 and Co_2O_3 are formed, but at a higher temperature these begin to turn into NiO and CoO (or to Ni_3O_4 and Co_3O_4, say some authorities).

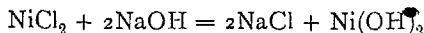
Problems 2, 3, 4, 5 and 6.—The oxidation of nickel and cobalt compounds.

2. As mentioned above, the nitrates, when ignited, leave *-ic* oxides in each case, Ni_2O_3 and Co_2O_3. With hot strong hydrochloric acid these both evolve chlorine and leave *-ous* salts.

$$2Ni(NO_3)_2 = Ni_2O_3 + 4NO_2 + O$$
$$Ni_2O_3 + 6HCl = 2NiCl_2 + Cl_2 + 3H_2O$$

Similarly for cobalt.

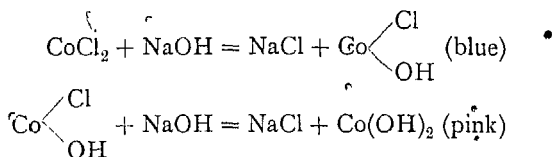
Co_2O_3, however, is less ready to evolve chlorine with dilute hydrochloric acid, and goes into solution mainly as a cobaltic salt (confirm by adding caustic soda).

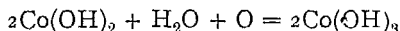
$$Co_2O_3 + 6HCl = 3H_2O + 2CoCl_3$$

3. The action of caustic soda on nickelous salts is to precipitate the green hydroxide, insoluble in excess.

$$NiCl_2 + 2NaOH = 2NaCl + Ni(OH)_2$$

With cobaltous salts, a blue precipitate is first produced,

turning pink with more caustic soda; the blue precipitate is well known as a basic salt—

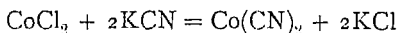
$$CoCl_2 + NaOH = NaCl + Co\begin{matrix}/Cl \\ \backslash OH\end{matrix} \text{ (blue)}$$

$$Co\begin{matrix}/Cl \\ \backslash OH\end{matrix} + NaOH = NaCl + Co(OH)_2 \text{ (pink)}$$

On shaking up each hydroxide with air, the pink cobaltous hydroxide is oxidised to brown cobaltic hydroxide, $Co(OH)_3$, thus—

$$2Co(OH)_2 + H_2O + O = 2Co(OH)_3$$

whereas nickelous hydroxide is not affected. Herein cobalt behaves more like iron than does nickel.

With other oxidising agents both cobaltous and nickelous hydroxides are oxidised to the corresponding -ic hydroxides. The equations may be left to the student.

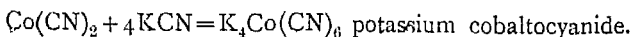
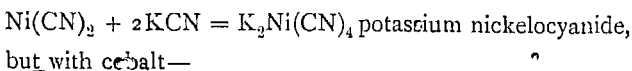
4. The action of potassium cyanide on nickel and cobalt salts is first to precipitate the cyanides, thus—

$$CoCl_2 + 2KCN = Co(CN)_2 + 2KCl$$

Similarly with nickel.

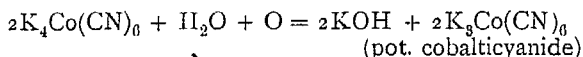
On adding more cyanides these precipitates redissolve. If equal volumes of equivalent solutions of nickel and cobalt are used, however, more potassium cyanide will be needed to dissolve the cobalt cyanide than the nickel cyanide. Roughly it should be found that the volume required by the cobalt : volume required by the nickel = 2 : 3. This must mean that in the case of the nickel, the reaction is—

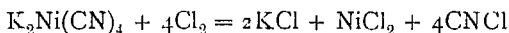
$Ni(CN)_2 + 2KCN = K_2Ni(CN)_4$ potassium nickelocyanide,

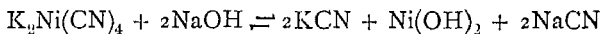
but with cobalt—

$Co(CN)_2 + 4KCN = K_4Co(CN)_6$ potassium cobaltocyanide.

(*Total* amounts of potassium cyanide required, including that for precipitation of the cyanide, are as 2 : 3.)

On boiling the solutions of the potassium nickelocyanide (colourless) and cobaltocyanide (brownish-yellow), nothing happens to the nickel, but the cobalt goes colourless. On testing with litmus, nothing is noticed in the case of the nickel; the cobalt solution is strongly alkaline.* This must mean that oxidation has taken place by atmospheric oxygen, thus—

$$2K_4Co(CN)_6 + H_2O + O = 2KOH + 2K_3Co(CN)_6$$
(pot. cobalticyanide)

Oxidising agents all have a similar effect on the cobaltocyanide solution, turning it to the colourless cobalticyanide. On the nickelocyanide they have an effect such as that shown below: *e.g.* with chlorine, the nickelocyanide is decomposed.

$$K_2Ni(CN)_4 + 4Cl_2 = 2KCl + NiCl_2 + 4CNCl$$

Moreover, caustic soda can, partly, at any rate, decompose nickelocyanide, thus—

$$K_2Ni(CN)_4 + 2NaOH \rightleftharpoons 2KCN + Ni(OH)_2 + 2NaCN$$

N.B.—*These reactions will* NOT *take place if excess of potassium cyanide be present with the nickelocyanide.*

If to the nickelocyanide, therefore, caustic soda, followed by bromine or chlorine water, be added, the nickelous hydroxide is oxidised to nickelic hydroxide, and the reaction shown above is able to complete itself, and the nickel is completely precipitated. These reagents, however, have *no effect* on the cobalticyanide, and no cobalt is precipitated. The method of separation is obvious then. To the *mixed* nickel and cobalt solutions add *just enough* potassium cyanide to redissolve the precipitate first formed. Now

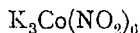
* Before boiling, the solutions should be *exactly* neutralised with dilute acetic acid, as any excess of KCN will react alkaline.

put into an open dish, and boil. The cobalticyanide is formed as above. Now add caustic soda, followed by bromine water [or better, pass in chlorine]. Nickelic hydroxide is precipitated. The cobalt is tested for in the filtrate by the borax bead.

Note that here again cobalt behaves just like iron, whilst the behaviour of nickel is quite different.

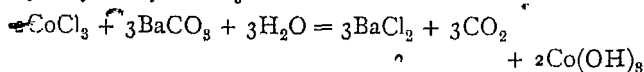
5. Here it will be noticed that a yellow precipitate is slowly formed. On analysis, it will be found to contain potassium, cobalt, and a nitrite. Note, however, that the substance does not show the usual reactions of cobalt, *e g.* with caustic soda, etc., and, therefore, no cobalt ions are present. Hence the cobalt must be present as a complex anion, and it has been shown to be in the cobaltic state.

Hence we decide that the cobalt is in the negative ion in a complex form, in the cobaltic state, and the substance is potassium cobaltinitrite, analogous to cobalticyanide—

$$K_3Co(NO_2)_6$$

The reactions involved in its formation may be left to the student, with the hint that the oxidation from the cobaltous to the cobaltic state is performed by free nitrous acid, thus—

$$2HNO_2 = H_2O + 2NO + O$$

6. Barium carbonate will not bring about the hydrolysis of nickelous and cobaltous salts like it does to ferric salts (see under Iron, Problem 8). But by the addition of bromine water the cobaltous salt gets oxidised to the cobaltic state, and the cobaltic salts, like the ferric salts, are readily hydrolysed by $BaCO_3$.

$$2CoCl_3 + 3BaCO_3 + 3H_2O = 3BaCl_2 + 3CO_2 + 2Co(OH)_3$$

The nickelous salt is *not* oxidised to nickelic, and consequently is not hydrolysed, as we have seen that salts of the divalent elements are not readily hydrolysed. Thus we see that in its reactions cobalt, forming salts corresponding to the oxide Co_2O_3, is much more like iron than is nickel, which forms no salts whatever corresponding to the oxide Ni_2O_3.

Problem 7.—The carbonates of nickel and cobalt.

When sodium carbonate solution, not too dilute, is added cold to nickelous or cobaltous salts, there will be *no carbon dioxide evolved*, and therefore the precipitates will be the *normal* carbonates $NiCO_3$ and $CoCO_3$.

Sodium bicarbonate produces the same precipitates. If the carbonate solution is hot and dilute, however, more or less basic carbonates will be produced.

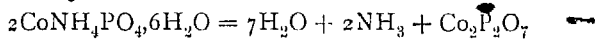
Ammonium carbonate produces basic carbonates also, even in strong solution.

A determination of the carbon dioxide in the normal carbonate should be made to confirm this.

Problem 8.—A double salt containing cobalt.

The purple precipitate will be found to be a double phosphate of cobalt and ammonium, containing water of crystallisation. Its crystalline form, under the microscope, will be found to be exactly similar to that of magnesium ammonium phosphate (*q.v.*), consisting of clusters of needles like stars.

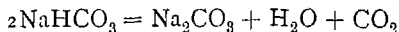
Its formula is exactly analogous to the magnesium salt, being $CoNH_4PO_4,6H_2O$, and on ignition it gives off ammonia and water, leaving cobalt pyrophosphate.

$$2CoNH_4PO_4,6H_2O = 7H_2O + 2NH_3 + Co_2P_2O_7$$

VOLUMETRIC PROBLEMS

A.—ACIDIMETRY AND ALKALIMETRY

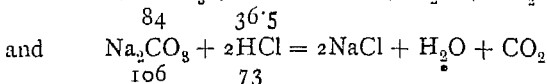
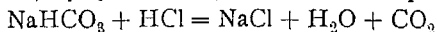
Problem 1.

The substance supplied was sodium bicarbonate, $NaHCO_3$. On ignition, it turns into the normal carbonate, Na_2CO_3.

$$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$$

With an acid, say hydrochloric, the actions are respectively*—

$$\underset{84}{NaHCO_3} + \underset{36{\cdot}5}{HCl} = NaCl + H_2O + CO_2$$

and

$$\underset{106}{Na_2CO_3} + \underset{73}{2HCl} = 2NaCl + H_2O + CO_2$$

Since 84 grams of $NaHCO_3$ neutralise 36·5 grams of HCl,

1 gram ,, ,, $\frac{36{\cdot}5}{84}$,, ,,

$= {\cdot}4345$,, ,,

and since 106 grams of Na_2CO_3 neutralise 73 grams of HCl,

1 gram ,, ,, $\frac{73}{106}$,, ,,

$= {\cdot}6886$,, ,,

Hence the volumes of N hydrochloric acid used by 1 gram of the bicarbonate and carbonate should be in the ratio of 4345 : 6886 = 1 : 1·125 nearly.

Since all normal solutions of acids are of equivalent strength, the same volume relation will be found to hold for any acid used.

The method to be followed is to weigh out about 4 grams of the substance, transfer to a 100 c.c. flask, and dissolve, make up to 100 c.c., and titrate 25 c.c. at a time. Indicator, methyl orange.

* In calculated examples given, approximate atomic weights have been used. If your work is sufficiently accurate, use exact atomic weights. (See Introduction.)

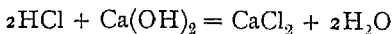
If litmus is used, the titration must be done at the boil. Whilst the titrations are being carried out, a further quantity of the substance is being ignited strongly in a *platinum* basin. Weigh out about 4 grams of the residue, and treat as above. Calculate the volumes of acid required to neutralise 1 gram of the dry substance in each case.

Problem 2.—*Determination of solubilities.*

Shake up an excess of each substance with warm water, cool down under the tap, take the temperature after standing for a few minutes, filter into a *weighed* graduated flask, and weigh. Make up to the mark, and titrate an aliquot portion with (1) $\frac{N}{25}$ hydrochloric acid; (2) $\frac{N}{10}$ hydrochloric acid; (3) N hydrochloric acid; (4) N caustic soda; (5) N hydrochloric acid. From results calculate weight of each substance that 100 grams of water will dissolve.

Example.—A saturated solution of slaked lime, $Ca(OH)_2$, was made, and 40 grams of it were weighed into a 100 c.c. graduated flask, made up to 100 c.c. with distilled water, and 25 c.c. at a time titrated with $\frac{N}{25}$ hydrochloric acid. Each 25 c.c. will contain 10 grams of the original saturated solution.

The action being

$$\underset{2 \times 36 \cdot 5}{2HCl} + \underset{74}{Ca(OH)_2} = CaCl_2 + 2H_2O$$

we see that 36·5 grams HCl (1 litre N HCl) =
37 grams $Ca(OH)_2$

or 1 c.c. N HCl = ·037 grams $Ca(OH)_2$

$\therefore$ 1 c.c. $\frac{N}{25}$ HCl = $\frac{\cdot 037}{25}$ " "

= ·00148 " "

The titrations were—

(1) 9·9 c.c.; (2) 10·0 c.c.; (3) 10·1 c.c. $\frac{N}{25}$ HCl

Mean = 10 c.c.

Since 10 c.c. $\frac{N}{25}$ HCl = ·00148 × 10 grams $Ca(OH)_2$
= ·0148 gram $Ca(OH)_2$

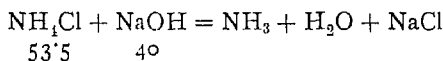
this weight of lime is contained in 10 *grams* of the saturated solution, or 10 grams of the solution contain—

·0148 gram lime,
9·9852 ,, water.

Hence calculate the weight of slaked lime in 100 grams of water. This is the solubility.

Problem 3.—Determination of ammonium chloride.

The principle of this problem is to turn out the ammonia from the chloride by a known excess of N caustic soda, and to find out how much is left over. The difference between the amount added and amount left is the amount used up in the reaction—

$$\underset{53\cdot5}{NH_4Cl} + \underset{40}{NaOH} = NH_3 + H_2O + NaCl$$

The ammonia, of course, is boiled off, and the solution then titrated with N acid.

Method.—Dissolve about 5 grams of ammonium chloride in water. Make up to 250 c.c. and shake. Measure out three lots of 25 c.c. each of the ammonium chloride solution into three flasks of about 150 c.c. capacity. To each add 25 c.c. of N caustic soda, and boil on a gauze till the escaping steam no longer turns red litmus paper blue. Then titrate with N acid, find out how many c.c. of the N caustic soda added are left. Suppose x c.c. are left, then $25 - x$ have been used in the above reaction.

Then since 1 c.c. N NaOH contains ·04 gram of NaOH,
1 c.c. N NaOH = ·0535 gram of NH_4Cl,

∴ $(25 - x)$ c.c. N NaOH = $(25 - x) \times$ ·0535 gram NH_4Cl,

and this is therefore the weight of ammonium chloride in 25 c.c. of the given solution. Hence calculate the weight of ammonium chloride per litre of solution.

Problem 4.—*Formula of washing-soda crystals.*

Find the weight of sodium carbonate in a known weight of the crystals by titrating with N acid. Calculate the percentage weights of carbonate and of water in the crystals.

Divide these numbers by the respective molecular weights. The results will be the molecular proportions in which the carbonate and water are combined. Reduce this ratio to its simplest whole numbers.

Example.—Suppose the percentage composition of the crystals is found to be—

$$Na_2CO_3(\text{M.W.} = 106) = 37{\cdot}07\ \%$$
$$H_2O(\text{M.W.} = 18) = 62{\cdot}93\ \%$$
$$\overline{100{\cdot}00\ \%}$$

then $\frac{37{\cdot}07}{106} = {\cdot}35$

and $\frac{62{\cdot}93}{18} = 3{\cdot}5$

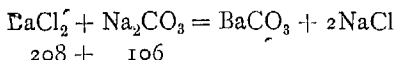
Hence the molecular ratios of Na_2CO_3 and H_2O are—

·35 molecule of carbonate and 3·5 molecules of water;
or 1 molecule of carbonate and 10 molecules of water,
i. e. Formula of crystals = $Na_2CO_3, 10H_2O$.

Problem 5.—*Determination of barium chloride.*

By adding a known excess of N sodium carbonate to a measured volume of the solution of barium chloride, and

titrating the excess, the weight of barium chloride present can be calculated from the equation—

$$\underset{208}{BaCl_2} + \underset{106}{Na_2CO_3} = BaCO_3 + 2NaCl$$

	106 grams Na_2CO_3	react with	208 grams	$BaCl_2$
	53 ,, ,,	,,	104 ,,	,,
i. e.	1 litre of N Na_2CO_3	,,	104 ,,	,,
∴	1 c.c. N Na_2CO_3	,,	·104 ,,	,,

Proceed thus: 25 c.c. of the barium solution (which should be about 1·5 normal) are measured by means of a pipette into a 100 c.c. graduated flask, and N sodium carbonate is then added up to the mark (*i. e.* 75 c.c. N carbonate are added). Shake, and filter through a *dry* filter into a *dry* vessel, rejecting the first few c.c. that come through. (Why?) Titrate 25 c.c. of this filtrate at a time with N acid, using methyl orange as indicator. Calculate how many c.c. of N carbonate are left out of the 75 added. Obviously this will be four times that left in the 25 c.c. titrated. Let this volume be x c.c.

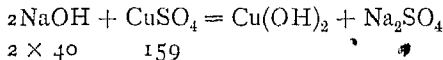
Then $(75 - x) =$ vol. of N carbonate used up by the barium chloride.

∴ $(75 - x) \times \cdot 104 =$ Weight of barium chloride per 25 c.c. of solution. Hence calculate weight per litre.

Problem 6.—*Determination of copper sulphate.*

The method used here is precisely similar to that used in the previous problem (No. 5), except that the copper sulphate is precipitated with a known excess of N caustic soda, *not* sodium carbonate. The reason for this is that the carbonate precipitates a basic carbonate of copper, the composition of which varies according to dilution, temperature, etc., and hence we cannot set down a definite equation.

But

$$2NaOH + CuSO_4 = Cu(OH)_2 + Na_2SO_4$$
$$2 \times 40 \qquad 159$$

is quite definite.

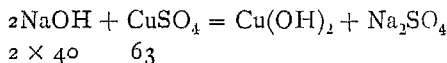
Since 40 grams NaOH (1 litre N NaOH) = 79·5 grams $CuSO_4$,

1 c.c. N NaOH = ·0795 gram $CuSO_4$.

Proceed as in Problem 5.

Problem 7.—Determination of the percentage of copper in a copper salt.

Weigh out about 5 grams of the salt, dissolve in a *little* water in a 100 c.c. flask. Cool, and add 75 c.c. of N caustic soda. Make up to mark with water, and proceed exactly as in Problem 6. The equation

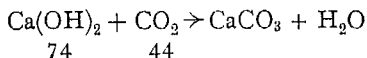
$$2NaOH + CuSO_4 = Cu(OH)_2 + Na_2SO_4$$
$$2 \times 40 \qquad 63$$

shows us that 1 litre of N caustic soda will precipitate 31·5 grams of copper as $Cu(OH)_2$. Hence the weight of copper in the weight of copper sulphate crystals taken can be found.

Problem 8.—Determination of the percentage of carbon dioxide in the atmosphere.

First find the volume of the Winchester bottle by filling with water, and pouring it out into a graduated cylinder. Now measure into the bottle 100 c.c. of the lime-water, stopper it up, and shake for several minutes. Stand aside. Meanwhile titrate the lime-water against the standard acid $\left(\frac{N}{25}\right)$ to find its exact strength.

Now pour the lime-water from the Winchester into a 250 c.c. graduated flask. Wash out the Winchester with

several small quantities of water, add them to the contents of the flask, and make up to the mark. Titrate 50 c.c. (*i.e.* one-fifth) at a time with the $\frac{N}{25}$ acid (indicator, phenolphthalein), and find out how much calcium hydroxide has been used up in—

$$\underset{74}{Ca(OH)_2} + \underset{44}{CO_2} \rightarrow CaCO_3 + H_2O$$

Since 74 grams $Ca(OH)_2$ = 44 grams CO_2
= 22240 c.c. of CO_2

calculate what volume of carbon dioxide 1 c.c. of your lime-water is equivalent to. This multiplied by the *total* volume of lime-water left out of the 100 c.c. used = volume of carbon dioxide in the volume of the Winchester *minus* 100 c.c. (volume of lime-water added). Hence calculate the percentage volume in the air.

Problem 9.—*Determination of the vapour density of hydrochloric acid.*

Fix up the apparatus shown in Fig. 21, and collect the tube **B** full of hydrochloric acid gas. The gas is generated from 100 grams of salt, 100 grams of strong sulphuric acid, and 50 grams of water. This mixture gives a steady stream of gas on heating, under perfect control. The gas is dried by strong sulphuric acid in the wash-bottle. When **B** is full, close the taps and immediately disconnect from the apparatus. The HCl gas is now absorbed by opening one of the taps under water, which will rush up and fill **B** as soon as a drop or two have entered. There will always be a small bubble of air left, the volume of which can be found by running in water from a burette. Needless to say, the temperature and pressure of the gas in **B** should be known. Now wash the contents of **B** into a 250 c.c. graduated flask,

make up to the mark, and titrate 50 c.c. at a time with $\frac{N}{10}$ alkali, using a drop of methyl orange as indicator. The *weight* of hydrochloric acid in **B** is then known. The volume of **B** is also known, hence the vapour density, which will be the weight of this volume divided by the weight of

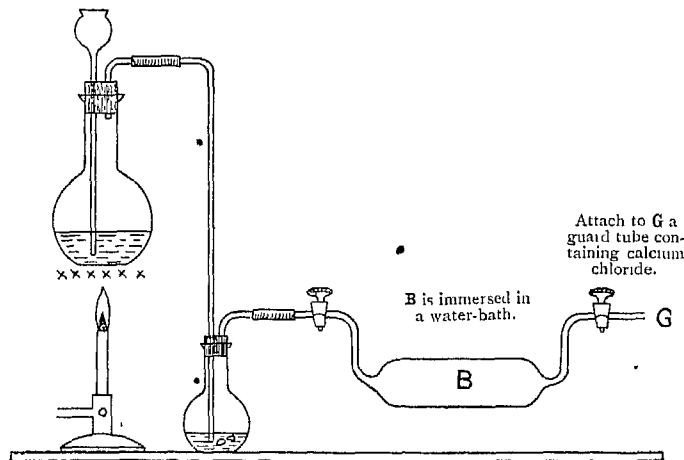



FIG. 21.

the same volume of hydrogen under the same conditions of temperature and pressure.

Problem 10.—*Determination of the equivalent of zinc.*

A known weight of pure zinc foil is put into a graduated flask and dissolved in a known excess of N acid. Fifty c.c. will be sufficient for 1 gram of zinc. The contents of the flask are made up to the mark with water (100 c.c. will be enough in the above case), and the excess of acid titrated in an aliquot portion (use 25 c.c. at a time here), with *methyl orange* as indicator. From the amount of acid left the

amount used by the zinc can be found, and hence the weight of zinc that will turn out 1 gram of hydrogen. [Remember that 1 c.c. of N acid contains ·001 gram of acid hydrogen.]

The equivalent of magnesium can be similarly found.

Problem 11.—*The ratio of the equivalents of two metals.*

A weighed portion of each metal is dissolved in a known excess of N acid, and the excess of acid found as in Problem 10. Find the ratio of the volumes of acid used by 1 gram of each metal.

These volumes will obviously be in the ratio of the *weights of hydrogen* displaced by 1 gram of the metals, and these weights are obviously *inversely as the equivalents.* For if 1 gram of a metal A displaces twice as much hydrogen as a metal B, the equivalent of A is evidently *half* that of B.

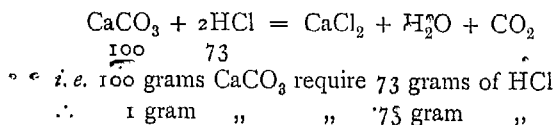
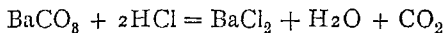
Problem 12.—*Determination of the percentage composition of a mixture of two carbonates.*

Find the volume (and therefore the weight) of normal acid (hydrochloric or nitric) that 1 gram of the given carbonate will neutralise. This is obviously best done by dissolving a weighed portion of the powder in a known excess of acid, and finding how much acid is left by titrating an aliquot part with N caustic soda, using methyl orange as indicator. [*N.B.*—Do *not* use N sodium carbonate. Why?] Hence follows the weight of hydrochloric or nitric acid required for 1 gram of the given carbonate. Now—

$$\underset{100}{CaCO_3} + \underset{73}{2HCl} = CaCl_2 + H_2O + CO_2$$

i. e. 100 grams $CaCO_3$ require 73 grams of HCl

∴ 1 gram " " ·73 gram "

And

$$BaCO_3 + 2HCl = BaCl_2 + H_2O + CO_2$$
$$\underset{197}{} \quad \underset{73}{}$$

i.e. 197 grams $BaCO_3$ require 73 grams of HCl

∴ 1 gram " " $\frac{73}{197}$ " "

= ·37 " "

If we find that 1 gram of the carbonate wants ·73 gram of hydrochloric acid (or an equivalent amount of nitric) it must be calcium carbonate. If 1 gram only requires ·37 gram of hydrochloric acid it must be barium carbonate. If the amount of acid required by the carbonate is intermediate between these two numbers, then the substance is a mixture of the two carbonates.

The percentage of each can be easily calculated as follows—

Let A be the weight of the mixed carbonates,

" B " " " hydrochloric acid required,

" x be the weight of $BaCO_3$ in the mixture.

Then $(A-x)$ is " " $CaCO_3$ " "

Since 1 gram of $BaCO_3$ requires ·37 gram of HCl

∴ x " " " ·37x " "

and since 1 gram of $CaCO_3$ " ·73 " "

∴ $(A-x)$ " " " ·73 $(A-x)$ "

Hence the quantity of hydrochloric acid required by the weight of mixture taken = ·37x + ·73 $(A - x)$.

But this = B, the weight found experimentally—

$$\therefore \cdot 37x + \cdot 73(A - x) = B.$$

Whence x is easily found, and $(A - x)$ follows. The percentages follow at once.

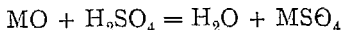
Problem 13.—*Basicity for an acid.*

Benzoic or oxalic acid may be supplied. Titrate a

known weight with N caustic soda and phenol-phthalein, and calculate the weight of the acid which neutralises 1 litre of N soda (*i.e.* 1 gram equivalent of caustic soda). This will be the equivalent of the acid. Its basicity is obviously $= \frac{\text{Molecular weight.}}{\text{Equivalent weight.}}$

Problem 14.—*Percentage composition of a metallic oxide.*

The weight of acid used by the metallic oxide must be calculated by titrating a known volume of the solution with N caustic soda (methyl orange) and finding how much of the 49 grams of sulphuric acid employed (*i.e.* weight per litre of N H_2SO_4) has been neutralised by the oxide. From this, calculate what weight of the oxide neutralises 49 grams of sulphuric acid. Let this be *W* grams. Since 49 grams of sulphuric acid contain 1 gram of hydrogen, and since this 1 gram of hydrogen has united with 8 grams of oxygen to form water—

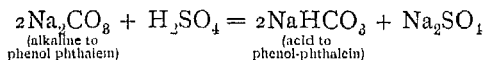
$$MO + H_2SO_4 = H_2O + MSO_4$$

therefore *W* grams of the oxide contain 8 grams of oxygen. Hence the percentage composition follows.

Problem 15.—*Analysis of sodium "sesquicarbonate."*

The salt given was sodium "sesquicarbonate." [This is sold as "sodium carbonate, silky crystals," by Messrs. Gallenkamp.]

Qualitative analysis will soon show that the substance is a carbonate of sodium. Since it gives off water and carbon dioxide on heating, it would appear to be sodium bicarbonate. Volumetric analysis, however, will show that this is *not* the case, as the amount of acid required to neutralise a known weight will *not* be that required for sodium bicarbonate. Moreover, the substance will be

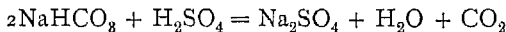
alkaline to phenol-phthalein, whereas sodium bicarbonate is acid to this indicator. Hence it must *also* contain some normal carbonate. The amounts of bicarbonate and carbonate contained can be found as follows. *If the solution is sufficiently dilute*, on adding acid the carbon dioxide evolved at first is absorbed by the normal carbonate left, to form bicarbonate, thus—

$$\underset{\text{(alkaline to phenol phthalein)}}{2Na_2CO_3} + H_2SO_4 = \underset{\text{(acid to phenol-phthalein)}}{2NaHCO_3} + Na_2SO_4$$

Hence to a *dilute* solution of a known weight of the salt [which is supplied] add a few drops of phenol-phthalein. Add N sulphuric acid till the pink colour just disappears. The carbonate is now converted to *bi*carbonate. [*N.B.*—If carbon dioxide escapes, the solution is too strong, and the next portion must be diluted.] Now add methyl orange, and run in more acid till the solution turns pink (methyl orange not being affected by carbolic acid).

From the volume of acid added to turn the phenol-phthalein colourless can be calculated the weight of normal carbonate present.

Since $2Na_2CO_3 + H_2SO_4 = 2NaHCO_3 + Na_2SO_4$, we see that IN THIS CASE 1 c.c of N $H2SO_4 = \cdot 0265$ gram Na_2CO_3.

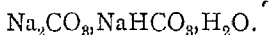
On adding methyl orange and more acid,

$$2NaHCO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2$$

or the same amount of acid is required to neutralise the bicarbonate formed from the normal carbonate as was required to turn the normal carbonate to the bicarbonate. Thus, if x c.c. of N acid were required to render the phenol-phthalein colourless, $2x$ c.c. are required completely to neutralise the normal carbonate present. If y c.c. was the TOTAL volume of acid added, then $(y - 2x)$ c.c. were used

to neutralise the bicarbonate *already* present. Hence follow the weights of both Na_2CO_3 and $NaHCO_3$ present in the weight of substance taken. Their sum is *less* than the weight of substance taken. The difference is therefore water of crystallisation.

Calculate the *percentages* of Na_2CO_3, $NaHCO_3$ and H_2O in the substance. Divide each number by the respective molecular weight. The numbers obtained will be the molecular ratios of the three substances. These should be in the ratio 1 : 1 : 1 of $Na_2CO_3 : NaHCO_3 : H_2O$.

Hence the formula of the substance is—

$$Na_2CO_3, NaHCO_3, H_2O.$$

Problem 16.—*Volumetric proof of the Law of Reciprocal Proportions.*

Having found the required numbers by methods similar to those of (*a*) Problem 10, (*b*) Problem 14, we shall have the following data—

(i) The weight of oxygen that combines with 1 gram of hydrogen.

(ii) The weight of zinc that displaces 1 gram of hydrogen.

(iii) The weight of zinc that combines with that weight of oxygen that combines with 1 gram of hydrogen.

Let these weights be respectively A, B, C.

The law of reciprocal proportions says that weights of elements which combine with or displace a given weight of another element are either the weights of these elements that combine with one another, or are simple multiples or sub-multiples of these weights. Do your weights A, B, and C bear this out?

[Regard Zinc and Oxygen as the elements combining with or displacing a given weight of hydrogen.]

Problem 17.—Determination of barium and ammonium chlorides in a solution containing both.

The barium chloride may first be estimated by precipitating with excess of N carbonate and finding how much is left over. (See Problem 5.) This must be done *quickly*, and *in the cold*, or loss of ammonia may result, since $Na_2CO_3 + 2NH_4Cl \rightarrow 2NaCl + (NH_4)_2CO_3$.

[Note that so long as the ammonium carbonate is kept in solution as such, it has the *same neutralising power* as the sodium carbonate from which it has been formed.]

The ammonium chloride may then be estimated as in Problem 3. The solution should not be too strong, however, or the excess of caustic soda will *precipitate* some barium hydroxide, $Ba(OH)_2$, whose solubility is somewhat limited. Any baryta so formed, however, will be *equivalent* to the caustic soda which causes its formation, and therefore possess the same neutralising power.

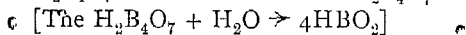
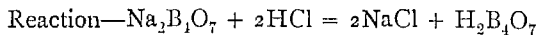
Problem 18.—Mixture of two acids.

1st method.—First find the volume of N alkali required for complete neutralisation. Then *to this neutral liquid* add a solution of barium chloride of known strength, and make up to a known volume.

Find the *excess of barium chloride* in an aliquot portion of this by the method of Problem 5, and hence calculate the weight of sulphuric acid in a known volume of the original solution. The weight of hydrochloric follows by difference.

2nd method.—Neutralise with N sodium CARBONATE, using methyl orange. Titrate this neutral liquid with $\frac{N}{10}$ silver nitrate, using potassium chromate solution as indicator. Hence calculate the amount of hydrochloric acid present. The sulphuric follows by difference.

Problem 19.—Standardisation of acids by means of borax.

Reaction—$Na_2B_4O_7 + 2HCl = 2NaCl + H_2B_4O_7$
[The $H_2B_4O_7 + H_2O \rightarrow 4HBO_2$]

If methyl orange be used as indicator, the end-point will be quite sharp, as boric acid has no effect on methyl orange. The use of litmus or phenol-phthalein is not permissible, because boric acid affects these indicators about as much as carbonic acid does in the titration of carbonates. But boric acid, being non-volatile, cannot be removed by boiling as can carbonic acid, and hence there is no sharp end-point with these indicators.

It will be found, moreover, that the solubility of borax at ordinary temperatures does not admit of a solution stronger than about $\frac{N}{2}$.

B.—ESTIMATIONS WITH $\frac{N}{10}$ $KMnO_4$.

Problem 1.—Determination of iron in a ferrous salt.

The iron may be present either in the ferrous, ferric, or both states. Which state is present must first be found. If ferrous, the usual precautions must be taken in getting it into solution, viz. air-free dilute sulphuric acid must be used, *cold*, and the solution must be made up to the required volume with air-free distilled water.

1 c.c. of $\frac{N}{10}$ $KMnO_4$ contains ·0008 gram of available oxygen = ·0056 gram Fe″.

For $2FeO + O \rightarrow Fe_2O_3$, or 16 grams of oxygen, oxidise 2×56 grams of ferrous iron.

If the substance supplied is iron wire, it must be dissolved in excess of dilute sulphuric acid at the boil. It must,

therefore, either be done in a stream of carbon dioxide, or the flask must be fitted with a Bunsen valve.

The estimation of iron in iron wire by means of permanganate generally gives high values, sometimes as much as 101 per cent. of iron. This is due to the carbon in the iron combining with the nascent hydrogen to give unsaturated hydrocarbons, which therefore take up a certain amount of permanganate. As it is all calculated as iron, the results are too high.

If the iron is in the ferric state, it must first be reduced to the ferrous state, before being made up to the required volume. (See Problem 2.)

If both ferrous and ferric states are present, see Problem 3.

Problem 2.—Determination of iron in a ferric salt.

In iron alum the iron is all in the ferric state. Hence, weigh out about 20 grams of the alum, dissolve in water, and make up to 250 c.c. Pipette out three or four lots of 25 c.c. each into some small flasks, add sulphuric acid, and several pieces of pure zinc. When completely reduced, allow the zinc to dissolve, or else remove it, and titrate with the $\frac{N}{10}$ permanganate.

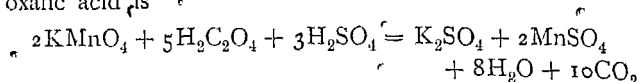
Problem 3.—Determination of iron in a mixture of ferrous and ferric salts.

If both ferrous and ferric iron are present, weigh out a portion, dissolve in air-free cold dilute sulphuric acid, make up to 250 c.c., and reduce the ferric iron to ferrous in several portions as above. Whilst waiting for the reduction to complete itself, find the ferrous iron in the usual way.

Then find the *total* iron in the reduced portions, and the amount of ferric iron will be the difference.

Problem 4.—*Determination of oxalic acid.*

The equation for the reaction between permanganate and oxalic acid is

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

A portion of the solution is measured out, excess of dilute sulphuric acid added, and the solution raised nearly to the boil before running in the permanganate, as the reaction goes very slowly in the cold.

Problem 5.—*Formula of potassium oxalate crystals.*

Find, by titrating weighed amounts of the crystals as above, the weight of $H_2C_2O_4$ in the crystals. The difference = water of crystallisation. Calculate the percentage of each, divide by the respective molecular weights, and so get molecular proportions. (See under Acids and Alkalis, Problem 4.)

Problem 6.—*Determination of calcium in a calcium salt by permanganate.*

The Iceland spar (about 1·5 grams) is dissolved in dilute hydrochloric acid in a beaker covered with a clock-glass. The latter is washed free from any solution that may have sprinkled up. The solution must now be made acid with acetic acid by first adding ammonia till alkaline, and then dilute acetic acid till acid. Then the solution is raised to a boil. Whilst boiling, boiling ammonium oxalate solution is added very slowly till precipitation is complete. Allow the precipitate to settle, filter, and transfer all the precipitate to the filter, washing with hot water till the washings no longer give a precipitate with silver nitrate. Now make a hole in the filter by means of a glass rod, and wash the precipitate into a 250 c.c. flask by a jet of hot

water from a wash-bottle. The last traces are washed off with hot dilute sulphuric acid. To the solution in the flask, which will be turbid with calcium sulphate, 20 c.c. of sulphuric acid (1 : 1) are added, the whole cooled, and made up to 250 c.c. with water. Remove 25 c.c. at a time, shaking up well before using the pipette, and titrate the oxalic acid with permanganate, as in Problem 5.

According to the equation in Problem 4—

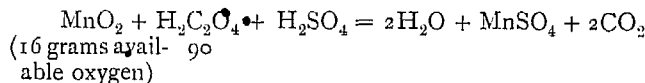
$2KMnO_4$ (= 5 atoms available O) oxidises $5H_2C_2O_4$ (5 × 90)
∴ 1 c.c. [= ·0008 gram of available O] oxidises ·0045 gram of oxalic acid,

and since this has been combined with ·0020 gram of calcium

$$\therefore \ 1 \text{ c.c. } \frac{N}{10} KMnO_4 = \cdot0020 \text{ gram Ca.}$$

Problem 7.—Determination of manganese dioxide in pyrolusite.

Not more than ·5 gram of the *finely powdered* pyrolusite is weighed into a 250 c.c flask. 100 c.c. (carefully measured) of $\frac{N}{10}$ oxalic acid are added, and some sulphuric acid. [25 c.c. of 1 : 4 acid.] The whole is now heated till no more black particles remain, cooled, made up to 250, and 50 c.c. at a time are titrated hot with $\frac{N}{10}$ permanganate, thus finding the *excess* of oxalic acid left. The amount used in the reaction :—

$$\underset{\text{(16 grams available oxygen)}}{MnO_2} + \underset{90}{H_2C_2O_4} + H_2SO_4 = 2H_2O + MnSO_4 + 2CO_2$$

is thus found.

Since 16 grams of available oxygen, or 87 grams of pyrolusite, oxidise 90 grams of oxalic acid, we have—

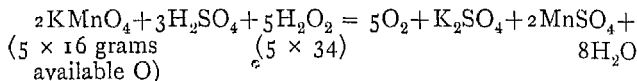
1 c.c. $\frac{N}{10}$ $K_2C_2O_4$ ($\cdot$0045 gram $H_2C_2O_4$) = $\cdot$0008 gram available oxygen
of = $\cdot$00435 gram MnO_2.

Problem 8.—*Determination of hydrogen peroxide.*

The reaction between permanganate and hydrogen peroxide is worked out thus.

Since $2KMnO_4$ in acid solution furnishes 5O, and $5H_2O_2 \rightarrow 5H_2O + 5O$, these oxygen atoms combine by pairs, and we have—

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = 5O_2 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

(5 × 16 grams available O) (5 × 34)

i. e. 1 c.c. $\frac{N}{10}$ $KMnO_4$ ($\cdot$0008 gram available oxygen)

= $\cdot$0017 gram H_2O_2 (containing $\cdot$0008 of a gram of available oxygen, which measures $\cdot$5560 c.c. at N.T.P.).

Problem 9.

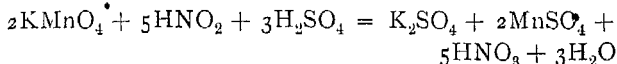
Titrate the permanganate against the oxalic acid in the usual way, the permanganate being added from the burette. Since $\cdot$0008 gram of available oxygen oxidises 1 c.c. of $\frac{N}{10}$ oxalic acid, the weight of available oxygen follows at once.

Problem 10.—*Determination of a nitrite.*

Since nitrous acid is volatile, the neutral nitrite solution is put into the burette, and a measured volume of permanganate put into a flask, made strongly acid with dilute sulphuric acid, warmed to 40° C., and the nitrite run in,

taking the decolorisation of the permanganate as the end-point. As the action is slow towards the end, add the nitrite slowly.

$2KMnO_4$ [*i. e.* 5O] will evidently oxidise $5HNO_2$ to $5HNO_3$.

$$2KMnO_4 + 5HNO_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 5HNO_3 + 3H_2O$$

Since HNO_2 comes from KNO_2, we have

$$\begin{array}{cc} & 85 \\ 5O & = 5KNO_2 \\ 5 \times 16 & 5 \times 85 \end{array}$$

$\therefore$ 1 c.c. $\frac{N}{10}$ $KMnO_4$(·0008 gram oxygen) = ·00425 gram KNO_2
or = ·00235 gram HNO_2.

Problem 11.—*Mixture of oxalic and sulphuric acids.*

The oxalic acid is first determined by measuring out 25 c.c., adding some H_2SO_4 (in case not enough is already present), and titrating hot with $\frac{N}{10}$ permanganate. The number of c.c. required will be equal to the number of c.c. of $\frac{N}{10}$ oxalic acid present in the 25 c.c. taken.

Now, using litmus or phenol-phthalein as indicator, find the total acidity by running in N *caustic soda.* (*N.B.*—If sodium carbonate is used, the titration must be carried out *at the boil*, with *litmus*, as methyl orange does not give a very sharp end-point with oxalic acid.)

The amount of oxalic acid being known, the amount of sulphuric follows at once.

Example—

Suppose 25 c.c. of the solution requires 3[illegible] c.c. of $\frac{N}{10}$ permanganate.

Then 25 c.c. of the solution are equivalent to—

$$30 \text{ c.c. } \frac{N}{10} \text{ oxalic acid,}$$
or 3 c.c. N oxalic acid,
$= 3 \times \cdot045$ grams oxalic acid,
$= \cdot135$,, ,, ,,

Hence follows the weight per litre.

Further—

Suppose 25 c.c. of the mixture require 36 c.c. of N caustic soda.

Then 25 c.c. of the mixture are equivalent to 36 c.c. of normal acid. Of these, 3 c.c. have been found to be oxalic, therefore 33 c.c. are N sulphuric.

∴ Weight of sulphuric acid per 25 c.c. $= 33 \times \cdot049$ gram
$= 1\cdot617$ gram.

Hence the weight per litre.

Problem 12.—*Mixture of ferrous oxalate and oxalic acid.*

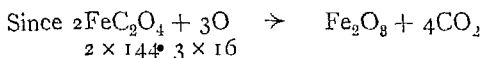
Find the number of c.c. of $\frac{N}{10}$ permanganate required to oxidise *completely* everything in a measured volume of the solution.

Now oxidise the iron in a measured volume by adding some dilute sulphuric and strong nitric acids, and boiling till oxidation is complete and nitr*ous* fumes formed have been driven off. Then titrate again with $\frac{N}{10}$ permanganate. The amount required this time is a measure of the *total* oxalic acid. The difference between this and the first titration is the amount required for the iron. The amount of oxalic acid in the free state follows at once.

Example—

Suppose 10 c.c. of the solution require 80 c.c. $\frac{N}{10}$ permanganate for complete oxidation.

After oxidation of the iron in 10 c.c., suppose 70 c.c. are now required. Then 10 c.c. were required for the iron. Also since $2KMnO_4$ oxidises 10Fe, and since $2KMnO_4$ oxidises $5H_2C_2O_4$, and since 10Fe requires $10H_2C_2O_4$ to form ferrous oxalate, the oxalic acid combined with the ferrous iron requires twice as much $KMnO_4$ as the iron itself. Hence, of the 80 c.c. of permanganate, 30 c.c. were required by the ferrous oxalate, and 50 c.c. were therefore required for the *free* oxalic acid.

$$\text{Since } \underset{2 \times 144}{2FeC_2O_4} + \underset{3 \times 16}{3O} \rightarrow Fe_2O_3 + 4CO_2$$

$$\therefore \ 1 \text{ c.c.} \frac{N}{10} KMnO_4 (= \cdot 0008 \text{ gm. O}) = \frac{2 \times 144}{6 \times 10^4} \text{ gms. } FeC_2O_4$$

$$= \cdot 0048 \text{ gm } FeC_2O_4$$

$\therefore$ 30 c.c = 30 × ·0048 gram FeC_2O_4, which is contained in 10 c.c. of solution. Hence weight of ferrous oxalate per litre.

And since 1 c.c. $\frac{N}{10}$ permanganate = ·0045 gram of $H_2C_2O_4$;

$\therefore$ weight of *free* oxalic acid in 10 c.c. of solution = ·0045 × 50 grams. Hence weight per litre.

Another method is as follows—

(*a*) Find total permanganate required as before.

(*b*) To another portion add sulphuric acid, completely oxidise by a little *strong* $KMnO_4$ solution (to avoid undue dilution), and *reduce* the iron back to the ferrous state by nascent hydrogen (any excess of permanganate being reduced at the same time).

Now titrate the amount of iron, and calculate the amount of $\frac{N}{10}$ permanganate required to oxidise it completely when in the form of ferrous oxalate. The difference between this

and the total permanganate required will be the volume required for the free acid.

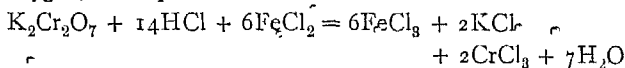
C.—POTASSIUM DICHROMATE PROBLEMS.

Problem 1.—*The formula of magnetite.*

Dissolve about 3 grams of the oxide (which need *not* be accurately weighed, as the ratio only of the two quantities of iron it contains is required) in some strong hydrochloric acid in a 250 c.c. graduated flask. Arrangements must be made to pass a stream of carbon dioxide through the flask *during solution and subsequent cooling.* Make up to the mark with *air-free water.* Titrate 50 c.c. at a time with potassium dichromate, using potassium ferricyanide as outside indicator in the usual way. This gives the ferrous iron. Whilst these titrations are being made, a further quantity of 25 c.c. is being reduced by nascent hydrogen. Titration of this gives the *total* iron in the *same* weight of Fe_2O_3. The difference between these two is the ferric iron. These should be in the ratio 1 : 2.

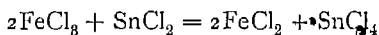
If preferred, reduction can be accomplished by adding stannous chloride solution to the ferric salt. A *slight excess only* should be used. Reduction is immediate. The excess of stannous chloride must be got rid of by adding mercuric chloride solution in slight excess, and titrate at once. The precipitate of mercurous chloride need *not* be filtered off.

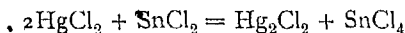
Reaction.—Since $K_2Cr_2O_7$ contains 3 atoms of available oxygen, the equation will be—

$$K_2Cr_2O_7 + 14HCl + 6FeCl_2 = 6FeCl_3 + 2KCl + 2CrCl_3 + 7H_2O$$

See Problem 6 under Chromium.

As in the case of $\frac{N}{10}$ permanganate, $\frac{N}{10}$ dichromate is of such a strength as to contain ·8 gram of available oxygen per litre, so that 1 c.c. = ·0008 gram O = ·0056 gram Fe.

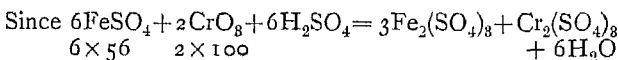
Reduction of ferric chloride by stannous chloride goes thus—

$$2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$$

The stannous chloride left over is oxidised thus—

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$

Problem 2.—*Estimation of chromic acid* (CrO_3).

The chromic acid being deliquescent is weighed thus. A stoppered weighing bottle containing some of the substance is weighed, about 1 to 1·5 grams are quickly tipped out into a 250 c.c. flask, and the bottle weighed again. The acid is dissolved in dilute sulphuric acid, and made up to the mark with water. Some is then put into a burette, and 25 c.c. of the standard iron solution are measured into a flask, and titrated in the usual way, with potassium ferricyanide as outside indicator.

[The process *may*, if desired, be reversed. How will the indicator work in this case?]

Since $\underset{6\times56}{6FeSO_4} + \underset{2\times100}{2CrO_3} + 6H_2SO_4 = 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 6H_2O$

we see that 1 c.c. of a N ferrous solution (*i. e.* such that it is oxidised to ferric sulphate by ·008 gram of oxygen) will be oxidised by—

$$\frac{2\times100}{6\times1000} \text{ gram of } CrO_3 \text{ (for } 2CrO_3 \text{ gives } 3O =$$

100

6 × 8 grams of oxygen)

$$= \cdot03333 \text{ grams of } CrO_3.$$

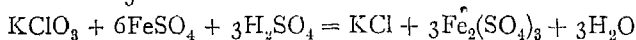
100

$\therefore$ 1 c.c. of $\frac{N}{5}$ $FeSO_4$ will be oxidised by ·00667 gram of CrO_3.

Hence the weight of CrO_3 in the weight of chromic acid taken can be found.

Problem 3.

Carefully weigh out about a gram of the chlorate, dissolve in air-free water in a 250 c.c. flask, and make up to the mark with air-free water. Transfer 25 c.c. to a flask, add a known excess of the $\frac{N}{5}$ ferrous solution, some air-free dilute sulphuric acid, and quickly titrate with $\frac{N}{10}$ $K_2Cr_2O_7$, thus finding the excess of ferrous salt. From this is found the volume of $\frac{N}{5}$ ferrous solution used in the action—

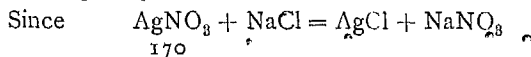
$$KClO_3 + 6FeSO_4 + 3H_2SO_4 = KCl + 3Fe_2(SO_4)_3 + 3H_2O$$

Since $KClO_3$(= 122·5) supplies 3 × 16 grams of available oxygen, and since 1 c.c. of $\frac{N}{5}$ ferrous solution is oxidised by ·0016 gm. of oxygen;

$$\therefore 1 \text{ c.c. of } \frac{N}{5} \text{ ferrous solution} = \frac{122{\cdot}5}{30{,}000} \text{ gram } KClO_3$$
$$= {\cdot}00408 \quad ,, \quad ,,$$

D.—ANALYSES BY $\frac{N}{10}$ SILVER NITRATE.

Problem 1.—*To find the equivalent of sodium.*

Weigh out about ·5 to ·75 of pure sodium chloride (see below), put into a 250 c.c. flask, dissolve in *distilled* water, and make up to the mark. Titrate 25 c.c. at a time, using a few drops of potassium chromate solution as indicator.

Since $\underset{170}{AgNO_3} + NaCl = AgCl + NaNO_3$

and $\frac{N}{10}$ silver nitrate contains 17 grams $AgNO_3$ per litre,

∴ 1 c.c. = ·00355 gram of chlorine.

Calculate the weight of sodium combined with 35·5 grams of chlorine.

The pure sodium chloride necessary for this experi-

ment is prepared as follows. The commercial article contains certain amounts of iron and magnesium salts. Hence dissolve about 200 grams of salt in about half a litre of water, and add about 10 c.c. of milk of lime. This precipitates the hydroxides of heavy metals. Now add about 3 grams of barium chloride dissolved in a little water. This precipitates any sulphates that may be present. Now add a solution of about 8 grams of sodium carbonate. This precipitates the excess of calcium and barium. Filter, and evaporate the filtrate till it is saturated. Cool, and saturate with hydrochloric acid gas. Pure sodium chloride is precipitated, which is filtered off on the pump, dried in the steam oven, and finally heated in a platinum basin.

Problem 2.—The equivalent of potassium.

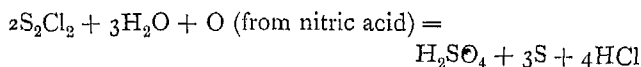
The preparation of pure potassium chloride is carried out precisely as for sodium chloride, except that at the end *potassium* carbonate is used to precipitate the calcium and barium. The purified potassium chloride is fused in a platinum basin, and whilst hot the basin is floated on some cold water, when the contraction of the metal will free the fused mass. Keep in a well-stoppered bottle. Carry out the estimation as with sodium chloride.

Problem 3.—Percentage composition of sulphur chloride.

Sulphur monochloride, S_2Cl_2, is made by passing dry chlorine over small lumps of sulphur heated in a retort, the neck of which passes into a flask kept cool under the tap. As the vapour is very pungent, the preparation should be done in the draught-cupboard. When the sulphur has all been converted into a liquid, a few small pieces more sulphur are added, and the liquid is distilled. The distillate is rectified, and the portion boiling at 138° C. collected separately. An air condenser is used, not a Liebig

condenser. Weigh out a small portion in a small weighed bulb blown on a piece of drawn-out tubing. The bulb is weighed empty, warmed gently, the neck introduced into a tiny beaker containing the monochloride, and allowed to cool. The end of the neck is sealed in the bunsen, and the whole weighed again.

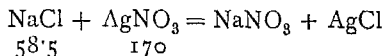
Place the bulb in a beaker containing plenty of dilute nitric, and break it by means of a glass rod. The chloride is decomposed thus—

$$2S_2Cl_2 + 3H_2O + O \text{ (from nitric acid)} = H_2SO_4 + 3S + 4HCl$$

Warm, filter, wash the filter with warm water, and make up the filtrate and washings to some convenient volume.

Remove an aliquot portion and exactly neutralise with N sodium carbonate (*not* caustic soda, as this generally contains a little sodium chloride). Now add a few drops of potassium chromate, and titrate the chlorine with $\frac{N}{10}$ silver nitrate. From your results, calculate the percentage of sulphur and chlorine in the substance.

Problem 4.—*Mixture of potassium and sodium chloride.*

If the substance is pure sodium chloride, since

$$\underset{58 \cdot 5}{NaCl} + \underset{170}{AgNO_3} = NaNO_3 + AgCl$$

∴ 1 gram of sodium chloride requires $\frac{170}{58 \cdot 5}$ grams silver nitrate

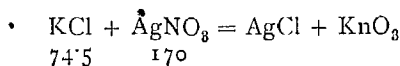
$$= \frac{1 \text{ litre of N silver nitrate}}{58 \cdot 5}$$

$$= \frac{10 \text{ litres } \frac{N}{10} \text{ silver nitrate}}{58 \cdot 5}$$

$$= 170 \cdot 9 \text{ c.c. } \frac{N}{10} \text{ silver nitrate}$$

then 1 gram of your substance will require 170·9 c.c. of $\frac{N}{10}$ silver nitrate.

If it is pure potassium chloride, since

$$\underset{74·5}{KCl} + \underset{170}{AgNO_3} = AgCl + KnO_3$$

∴ 74·5 grams potassium chloride require 170 grams (1 litre of normal) silver nitrate.

$$\therefore \quad 1 \text{ gram KCl requires } \frac{10 \text{ litres of } \frac{N}{10} AgNO_3}{74·5}$$

$$= 134·2 \text{ c.c. } \frac{N}{10} AgNO_3$$

then 1 gram of your substance will require 134·2 c.c. of $\frac{N}{10}$ gNO_3.

Carry out the titrations just as in Problem 1 and calculate the volume of $\frac{N}{10}$ silver nitrate required for 1 gram of the substance.

If this is 170·9 c.c., it must be pure sodium chloride.

" " 134·2 c.c., " " " potassium chloride.

If the volume is intermediate between these two numbers, the substance is a mixture of the two chlorides.

The percentage of each is found thus. Let A be the weight of substance taken, and B the number of c.c. of $\frac{N}{10}$ silver nitrate required for 1 gram. Let x be the weight of potassium chloride, then $(A - x)$ is the weight of sodium chloride in the weight A of the mixture taken.

Since 1 gram of KCl requires 134·2 c.c. $\frac{N}{10}$ $AgNO_3$

and since 1 gram of NaCl requires 170·9 c.c. of $\frac{N}{10}$ $AgNO_3$

∴ (A − x) ,, ,, 170·9 (A − x) ,, ,,

∴ Total volume of $\frac{N}{10}$ $AgNO_3$ required

$$= 134·2 \times x + 170·9 (A - x)$$
$$= B.$$

From this equation x and A − x follow at once, and hence the percentage weight of each salt in the mixture.

Problem 5.—*Determination of a mixture of hydrochloric and sulphuric acids.*

Titrate the solution with N sodium *carbonate*, using methyl orange, for the total acid. To the solution thus neutralised add a few drops of potassium chromate, and titrate the hydrochloric acid with $\frac{N}{10}$ silver nitrate. Hence follows the weight of sulphuric acid.

Example—

25 c.c. of the solution required 30 c.c. of N Na_2CO_3

∴ 25 ,, ,, ,, is equivalent to 30 c.c. of N acid.

The same solution now requires 30 c.c. of $\frac{N}{10}$ $AgNO_3$

or 3 c.c. of N $AgNO_3$

∴ 25 c.c. of the original solution contained 3 c.c. of N HCl

= 3 × ·0365 grams HCl.

Hence the weight of hydrochloric acid per litre.

Also the total acidity was = 30 c.c. of N acid.

Of this, 3 c.c. was N HCl

∴ 27 c.c. was N H_2SO_4

∴ weight of H_2SO_4 per 25 c.c. of solution = 27 × ·049 grams H_2SO_4

Hence the weight of sulphuric acid per litre.

Problem 6.—*Mixture of sodium chloride and hydrochloric acid.*

The solution is first titrated with $\frac{N}{10}$ sodium *carbonate*, using methyl orange. This gives the hydrochloric acid. This neutral solution is then titrated with $\frac{N}{10}$ silver nitrate, giving the total chlorine. Of this, some was originally present as hydrochloric acid, therefore the rest was originally present as sodium chloride.

Example—

25 c.c. of the solution required 33 c.c. of $\frac{N}{10}$ Na_2CO_3
= 3·3 c.c. of N Na_2CO_3

∴ 25 c.c. of the solution contained 3·3 × ·0365 grams of HCl.

The same solution now requires 50 c.c. of $\frac{N}{10}$ $AgNO_3$
= 5 c.c. of N $AgNO_3$

∴ the solution is now equivalent to 5 c.c. of N NaCl

Of this 5 c.c., 3·3 c.c. were originally N HCl, giving of course 3·3 c.c. of N NaCl when neutralised;

∴ 25 cc. of the original solution contained—
5 − 3·3 c.c. N NaCl
= 2·7 c.c. N NaCl
= 2·7 × ·0585 grams NaCl

Hence weight of sodium chloride per litre.

Problem 7.—*The equivalent of bromine.*

Find the percentage of bromine in pure potassium bromide by titration with $\frac{N}{10}$ silver nitrate.

Calculate from your results the weight of bromine that combines with 39 grams of potassium. The result should be 80.

Problem 8.—*The equivalent of iodine.*

Perform this in a precisely similar manner to Problem 7, using potassium iodide.

Problem 9.—*Analysis of a mixture of silver and potassium nitrates.*

A known weight of the mixture is dissolved in distilled water and made up to a known volume. A burette is filled with this solution and run into a known volume of $\frac{N}{10}$ sodium chloride, using potassium chromate as indicator.

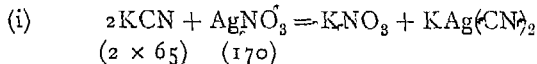
$$1 \text{ c.c. of } \frac{N}{10} \text{ NaCl} = \cdot 0170 \text{ gram } AgNO_3$$

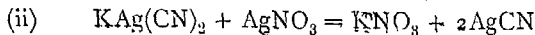
N.B.—Do not attempt to run the $\frac{N}{10}$ sodium chloride into the silver solution—the indicator will not work backwards accurately.

In all titrations with silver in neutral solution, the silver must be in the burette.

Problem 10.—*Action of potassium cyanide on silver nitrate.*

It is noticed that on adding the nitrate to the cyanide (*not vice versa*) a precipitate of silver cyanide, AgCN, momentarily forms, which immediately dissolves in excess of the cyanide. This is due to the formation of the soluble double cyanide $KAg(CN)_2$, thus—

$$\text{(i)} \qquad \underset{(2 \times 65)}{2KCN} + \underset{(170)}{AgNO_3} = KNO_3 + KAg(CN)_2$$

When *all* the free potassium cyanide has been converted into this double salt, the next drop of silver nitrate gives a permanent precipitate of silver cyanide, thus—

$$\text{(ii)} \qquad KAg(CN)_2 + AgNO_3 = KNO_3 + 2AgCN$$

The first appearance of the permanent precipitate indicates that reaction (i) is at an end, and that reaction (ii) is just ready to commence.

Hence we can estimate alkali cyanides by running in decinormal silver nitrate till the first appearance of a permanent precipitate. With care the end-point is absolutely sharp.

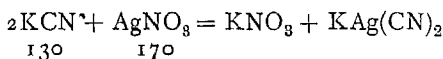
From equation (i) above, we see that—

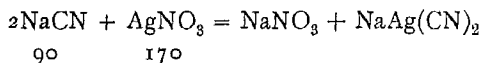
$$1 \text{ c.c. of } \frac{N}{10} AgNO_3 = \cdot 0130 \text{ gram KCN}$$

Problem 11.

The method is to find the number of c.c. of $\frac{N}{10}$ silver nitrate required by 1 gram of the substance.

If it were pure potassium cyanide, 1 gram would require 76·9 c.c. of $\frac{N}{10}$ $AgNO_3$.

$$\underset{130}{2KCN} + \underset{170}{AgNO_3} = KNO_3 + KAg(CN)_2$$

If it were pure sodium cyanide, 1 gram would require 102 c.c. of $\frac{N}{10}$ $AgNO_3$.

$$\underset{90}{2NaCN} + \underset{170}{AgNO_3} = NaNO_3 + NaAg(CN)_2$$

One gram of the mixed cyanides will require a volume of $\frac{N}{10}$ $AgNO_3$ intermediate between these two numbers.

Let x = weight of KCN in the weight of mixture taken (A grams). Then $(A - x)$ = weight of NaCN. Let V = volume of $\frac{N}{10}$ $AgNO_3$ required by this A grams of the mixture.

Then x grams of KCN require $x \times 76{\cdot}9$ c.c. of $\frac{N}{10}$ $AgNO_3$

$(A-x)$,, NaCN ,, $(A-x)$ 102 c.c. of $\frac{N}{10}$ $AgNO_3$

$\therefore 76{\cdot}9\,x + 102\,(A - x) = V.$

Hence x and $(A - x)$.

E.—ANALYSES BY $\frac{N}{10}$ NH_4CNS.

Problem 1.—*Analysis of coinage silver.*

Thoroughly clean the coin by warming it with—

(*a*) NaOH solution to free it from grease.

(*b*) Dilute HCl to free it from NaOH.

Wash thoroughly with distilled water, dry on filter-paper, and weigh.

Put it carefully into a 250 c.c. flask, and dissolve in a little nitric acid (1 : 1), with aid of heat if necessary.

Make up to the mark with distilled water, and titrate 25 c.c. at a time with $\frac{N}{10}$ NH_4CNS, using 1 c.c. of iron alum solution as indicator. (*N.B.*—The iron alum must, of course, be free from chloride.)

Problem 2.—*Percentage composition of hydrobromic acid.*

Add excess of $\frac{N}{10}$ silver nitrate to a weighed amount of the solution, which must be of known strength. Titrate the excess of silver ith $\frac{N}{10}$ thiocyanate.

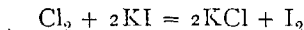
N.B.—The weight of hydrobromic acid in a given weight of solution is obtained by absorbing the gaseous acid in a flask whose weight, together with the delivery tubes and water, must be known. Weigh again after the absorption of HBr. If this solution be then diluted to a known

volume, and an aliquot part taken for titration, the *weight* of acid taken will be known.

F.—ANALYSES WITH $\frac{N}{10}$ IODINE AND $\frac{N}{10}$ THIOSULPHATE

Problem 1.—*Valuation of chlorine water.*

A measured amount (5 c.c. may be enough) of the chlorine water is added to excess of a 10 per cent. solution of potassium iodide.

$$Cl_2 + 2KI = 2KCl + I_2$$

The iodine is now titrated with $\frac{N}{10}$ thiosulphate, adding starch solution as indicator *when the action is nearly finished.*

[*N.B.*—The preparation of the starch solution is important. Many students are content to have the blue "iodide of starch" floating about as a flocculent precipitate, owing to a carelessly made starch solution. This will not do at all, as it is very inaccurate, and high results will be obtained. Boil about 100 c.c. of water in a flask, and to the boiling water add, in a thin stream, about a gram or so of starch made into a cream with *cold* water. Filter the resulting solution, and use about 5 c.c. of it as an indicator.]

Since $2Na_2S_2O_3 = I_2 = Cl_2$

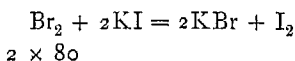
1 c.c $\frac{N}{10}$ thiosulphate = ·0127 gram I = ·00355 gram Cl.

Problem 2.—*To find the solubilities of bromine and iodine in water at the room temperature.*

(*a*) Prepare a saturated solution of bromine in water by shaking up a few c.c. of bromine with some cold water at the room temperature for several minutes. Allow to settle, pour off about 20 c.c. into a weighed 100 c.c. graduated flask, and weigh again. Difference = weight of *solution.*

Make up with water, shake and add 25 c.c. as quickly as possible to about 25 c.c. of 10 per cent. KI solution.

Titrate the iodine, calculate to bromine, multiply by 4 *i.e.* ($\frac{100}{25}$), and this will be the weight of bromine in the weight of solution originally taken. Hence calculate the weight of bromine *in* 100 *grams of water*—

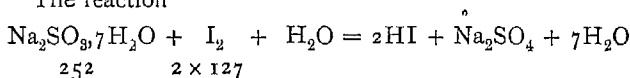
$$Br_2 + 2KI = 2KBr + I_2$$
$$2 \times 80$$

$\therefore$ 1 c.c. $\frac{N}{10}$ thiosulphate = ·0080 gram bromine.

(*b*) The solubility of iodine in water is found by making a saturated solution and titrating *directly* with thiosulphate. As the solubility is so small, $\frac{N}{100}$ thiosulphate will be necessary.

Details as to weighing out, etc., as in Problem 2 (*a*).

Problem 3.—*Estimation of sodium sulphite.*

The reaction

$$\underset{252}{Na_2SO_3,7H_2O} + \underset{2 \times 127}{I_2} + H_2O = 2HI + Na_2SO_4 + 7H_2O$$

is only complete with excess of iodine.

Hence weigh out about 3 grams of the crystalline sulphite, dissolve in cold recently boiled water, make up to 250, and take out 25 c.c. at a time. Add 50 c.c. of $\frac{N}{10}$ iodine, and titrate the *excess* of iodine *as quickly as possible* by $\frac{N}{10}$ thiosulphate.

Since 2 × 127 of iodine oxidise 252 grams of the *crystals*,

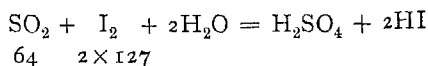
1 c.c. of $\frac{N}{10}$ iodine = ·0126 gram of $Na_2SO_3,7H_2O$.

Hence the percentage of sulphite.

This is rarely more than 90 per cent. owing to oxidation to sulphate by atmospheric oxygen during the preparation of the sulphite.

Problem 4.—*Estimation of sulphur dioxide in solution.*

Carry out on a similar principle to that in Problem 3. The sulphur dioxide solution may require considerably diluting before taking a measured portion.

$$\underset{64}{SO_2} + \underset{2 \times 127}{I_2} + 2H_2O = H_2SO_4 + 2HI$$

Only complete with excess of iodine.

From above equation

$$1 \text{ c.c. } \frac{N}{10} \text{ iodine} = \cdot 0064 \text{ gram } SO_2$$

Problem 5.—*Valuation of pyrolusite.*

The pyrolusite is heated with concentrated hydrochloric

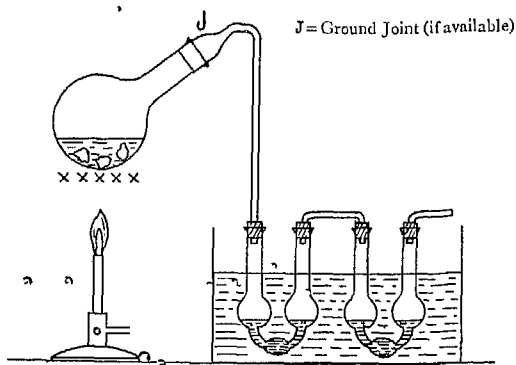
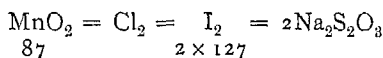



Fig. 22.

acid in a small flask, and the chlorine passed through two

bulb tubes containing excess of 20 per cent. potassium iodide solution. In order to sweep the last traces of chlorine out of the flask, some *lumps* of *native* magnesite, $MgCO_3$, are put into the flask, thus furnishing a steady stream of carbon dioxide throughout the reaction. The bulb tubes must be cooled during the experiment, as if they get warm, iodine will be lost by vaporisation. (*N.B.*—The upper bulbs must be *less* than half full.)

One gram of pyrolusite will be sufficient. At the end of the reaction wash the contents of the bulb tubes into a graduated flask, and make up to the mark, titrating about one fifth or one tenth at a time.

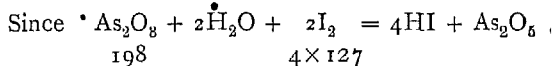
$$\underset{87}{MnO_2} = Cl_2 = \underset{2 \times 127}{I_2} = 2Na_2S_2O_3$$

$$\therefore 1 \text{ c.c. } \frac{N}{10} \text{ thiosulphate} = \cdot 00435 \text{ gram } MnO_2.$$

Problem 6.—Determination of arsenious oxide.

The hydriodic acid formed in the given reaction must be neutralised, or the reverse action will take place. The solution, however, must not be *alkaline*, as alkalis absorb iodine, forming iodides and hypoiodites. Sodium bicarbonate, however, does *not* react with iodine, and therefore this substance may be used to neutralise the hydriodic acid. It is somewhat difficult, however, to dissolve the oxide in bicarbonate solution, as it may not be heated, owing to decomposition in normal carbonate taking place.

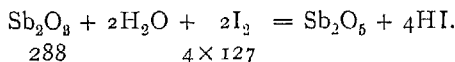
Hence, convert the arsenious oxide into sodium arsenite, Na_3AsO_3, by dissolving in as small an excess of caustic soda as possible. Just acidify this solution with dilute hydrochloric acid, and add a fair quantity of the saturated bicarbonate solution. Make up to a known volume, remove an aliquot portion, add some starch solution, and run in

$\frac{N}{10}$ iodine till the blue colour is permanent. *Or, better,* excess of iodine may be added and the excess titrated with $\frac{N}{10}$ thiosulphate.

$$\text{Since } \underset{198}{As_2O_3} + 2H_2O + \underset{4 \times 127}{2I_2} = 4HI + As_2O_5,$$

1 c.c. $\frac{N}{10}$ iodine = ·00495 gram As_2O_3.

Problem 7.—Estimation of antimony in tartar emetic.

Weigh out about 2 grams of the tartar emetic, dissolve in a little caustic soda (forming sodium antimonite), acidify with hydrochloric acid, add excess of sodium bicarbonate, and make up to 250 c.c. Take 25 c.c. at a time. Add a known excess of $\frac{N}{10}$ iodine, and titrate the excess with $\frac{N}{10}$ thiosulphate. The direct oxidation is very slow towards the end, except in presence of excess of iodine. Hence this method is much quicker than simply adding iodine till the oxidation is complete.

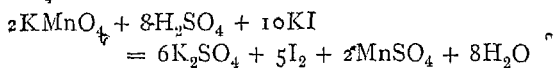
$$\underset{288}{Sb_2O_3} + 2H_2O + \underset{4 \times 127}{2I_2} = Sb_2O_5 + 4HI.$$

Hence

1 c.c. of $\frac{N}{10}$ iodine (= ·0127 gram I) = ·0072 gram Sb_2O_3
= ·0060 gram Sb.

Problem 8.—To standardise thiosulphate by means of $\frac{N}{10}$ permanganate.

We have already seen (Manganese, Problems 4*b* and 5)

that, since $2KMnO_4$ in *acid* solution gives $5O$, therefore $2KMnO_4$ will oxidise $10KI$.

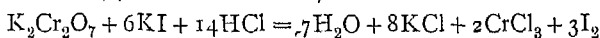
$$2KMnO_4 + 8H_2SO_4 + 10KI$$
$$= 6K_2SO_4 + 5I_2 + 2MnSO_4 + 8H_2O$$

Hence

1 c.c. of $\frac{N}{10}$ $KMnO_4$(= ·0008 gram O) = ·0127 gram I.

Hence, to standardise thiosulphate by $\frac{N}{10}$ permanganate, add 25 c.c. $\frac{N}{10}$ permanganate to excess of 10 per cent. of potassium iodide solution, acidified with hydrochloric acid. Run in the thiosulphate, using starch as indicator. If the thiosulphate is $\frac{N}{10}$, 25 c.c. are obviously required. If less are required, it is stronger than $\frac{N}{10}$. Calculate how much water to add. If more than 25 c.c. are required, it is weaker than $\frac{N}{10}$, and must either be made stronger and re-titrated, or the factor calculated.

Problem 9.—*To standardise thiosulphate by means of* $\frac{N}{10}$ *dichromate.*

Since $K_2Cr_2O_7$ in acid solution supplies $3O$ (see Problem 6(*d*) under Chromium) it will oxidise $6KI$, thus—

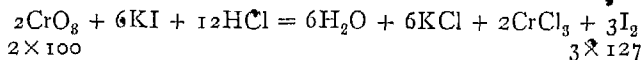
$$K_2Cr_2O_7 + 6KI + 14HCl = 7H_2O + 8KCl + 2CrCl_3 + 3I_2$$

Hence

1 c.c. $\frac{N}{10}$ $K_2Cr_2O_7$ = ·0127 gram I = 1 c.c. $\frac{N}{10}$ thiosulphate

Proceed therefore exactly as with permanganate in Problem 8, but remember that the end-point is a *little* difficult to determine at first, as the solution of chromic

chloride is pale green. A little experience will completely overcome this difficulty.

Problem 10.—*Estimation of* CrO_3 *in "battery chromic acid."*

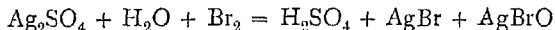
$$2CrO_3 + 6KI + 12HCl = 6H_2O + 6KCl + 2CrCl_3 + 3I_2$$
$$2 \times 100 \qquad\qquad 3 \times 127$$

Whence ·0127 gram iodine = ·00667 gram CrO_3

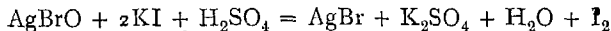
$\therefore$ 1 c.c. $\frac{N}{10}$ thiosulphate = ·00667 " "

Weigh out [as in Problem 2 under Potassium dichromate titrations] about 1 gram of the substance, dissolve in water, make up to 250 c.c., and take 25 c.c. at a time. Run into excess of 10 per cent. potassium iodide and acidify if necessary with hydrochloric acid (the "battery chromic acid" is already fairly strongly acid with the sulphuric acid used in its preparation). Titrate the liberated iodine with thiosulphate. The same difficulty with the end-point is met with here as in the previous problems.

Problem 11.—*Action of bromine on silver sulphate.*

When bromine water acts on silver sulphate solution it gives a precipitate of silver bromide, and the filtrate from this smells like bleaching powder, and bleaches litmus when acidified. Hence it must contain a hypobromite. The reaction would appear therefore to be—

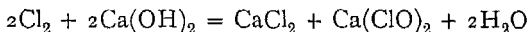
$$Ag_2SO_4 + H_2O + Br_2 = H_2SO_4 + AgBr + AgBrO$$

The reaction of silver hypobromite with potassium iodide is evidently—

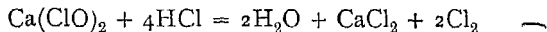
$$AgBrO + 2KI + H_2SO_4 = AgBr + K_2SO_4 + H_2O + I_2$$

i. e. the solution will turn out as much iodine from potassium iodide as will the bromine water added.

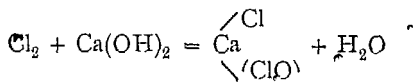
Confirm this by actual titrations.

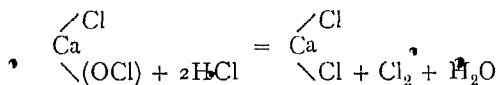
Problem 12.—*Action of chlorine on slaked lime.*

The slaked lime (about 20 grams) may be contained in a U-tube fitted with a calcium chloride tube to absorb the moisture given off. The increase in weight will be equal to the amount of chlorine absorbed. [*N.B.*—Sweep the chlorine out of the tubes by a stream of air before weighing.] To find the amount of *available* chlorine, make a weighed portion of the contents of the flask into a thin cream by grinding in a mortar with some pure water, and transfer to a 500 c.c. flask, washing out the mortar with water several times. Make up to the mark, shake well, and transfer an aliquot portion to a flask containing excess of 10 per cent. potassium iodide solution, render acid with hydrochloric acid, and titrate the iodine with $\frac{N}{10}$ thiosulphate. If carefully done, the weight of iodine liberated will be found equivalent to the weight of chlorine absorbed, which suggests—

$$2Cl_2 + 2Ca(OH)_2 = CaCl_2 + Ca(ClO)_2 + 2H_2O$$

This hypochlorite, treated with hydrochloric acid, gives a quantity of available chlorine equal to the total chlorine absorbed.

$$Ca(ClO)_2 + 4HCl = 2H_2O + CaCl_2 + 2Cl_2$$

which of course will liberate an equivalent amount of iodine from KI. But *no* $CaCl_2$ will be dissolved out of the powder by absolute alcohol. The chloride and hypochlorite must therefore be present as a *double salt*, this being the only alternative. Thus—

$$Cl_2 + Ca(OH)_2 = Ca\begin{matrix}/Cl \\ \backslash ClO\end{matrix} + H_2O$$

When this is acted on by hydrochloric acid, we have

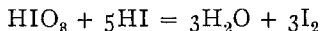
$$Ca\begin{cases}Cl\\(OCl)\end{cases} + 2HCl = Ca\begin{cases}Cl\\Cl\end{cases} + Cl_2 + H_2O$$

thus giving an amount of available chlorine equal to the chlorine absorbed.*

Problem 13.—*Action of bromine on slaked lime.*

It has lately been proved by L. G. Killby that bromine and calcium hydroxide form a true bleaching-powder, the bromide and hypobromite being in equivalent proportions. Carry out as in the previous problem. If excess of bromine be passed over, however, a dark red substance forms which contains very loosely combined bromine, and is probably a compound of calcium bromide and bromine analogous to KBr_3 and KI_3, the latter being a well-defined compound.

Problem 14.—*Action of iodic acid on hydriodic acid.*

A solution of *neutral* potassium iodate has no action on potassium iodide, but on acidifying, the liberated iodic acid reacts with the liberated hydriodic acid, thus—

$$HIO_3 + 5HI = 3H_2O + 3I_2$$

Hence, with a mixture of iodate and iodide, the addition of an acid will cause the liberation of iodine in accordance with this reaction. If the acid added is not in excess (*i.e.* with excess of iodate and iodide) the amounts of iodic and hydriodic acids liberated will adjust themselves so as to allow the above reaction to take place.

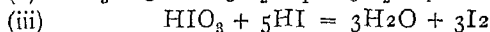
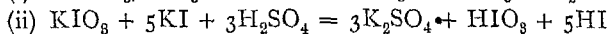
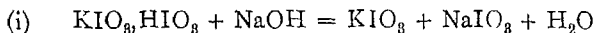
Since you are in this case supplied with the *acid* salt KIO_3,HIO_3, it is first necessary to neutralise a known volume exactly with the soda supplied. (Use methyl

* When bleaching powder dissolves in water, it has been shown that it *does* form a mixture of the hypochlorite and chloride.
$2Ca(OCl)Cl = CaCl_2 + Ca(OCl)_2$ *Cf.* action of chlorine on *dissolved* alkali.

orange.) Then add excess of potassium iodide and a measured volume of the sulphuric acid the strength of which is required. Such an amount of acid must be added that there is still some iodate left. This can obviously be done by titrating the acid against the alkali, and then employing say about six times the volume of acid equivalent to the soda required to neutralise the iodate solution. As will be seen from equations (i) and (ii), this will leave plenty of iodate over.*

(i) $KIO_3,HIO_3 + NaOH = KIO_3 + NaIO_3 + H_2O$

(ii) $KIO_3 + 5KI + 3H_2SO_4 = 3K_2SO_4 + HIO_3 + 5HI$

(iii) $HIO_3 + 5HI = 3H_2O + 3I_2$

These show us that $3I_2$ will be liberated by $3H_2SO_4$,

i.e. 6×127 grams of iodine $= 3 \times 98$ grams of sulphuric acid.

$\therefore$ 127 grams of iodine = 49 grams of sulphuric acid.

$\therefore$ 1 c.c. $\frac{N}{10}$ iodine = ·0049 gram of sulphuric acid.

The liberated iodine is titrated with $\frac{N}{10}$ thiosulphate in the usual way. Sufficient of the original solutions should be taken to be made up to, say, 250 c.c., so as to give several titrations for the one mixture.

N.B.—The acid iodate KIO_3,HIO_3 is often used to standardise thiosulphate with, by adding it to potassium iodide, acidifying and titrating the liberated iodine. It is used in preference to the neutral salt, as it is more easily obtained in a reliable state of purity.

* The volume of NaOH added to a given volume of iodate is seen to furnish enough iodate for 12 equivalent vols. of H_2SO_4. By using half this you will be on the safe side.

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